



## EUROPEAN PATENT APPLICATION

(43) Date of publication:  
17.07.1996 Bulletin 1996/29

(51) Int. Cl.<sup>6</sup>: C10M 169/04  
// C10N20:02, C10N40:04

(21) Application number: 96300227.4

(22) Date of filing: 11.01.1996

(84) Designated Contracting States:  
BE DE ES FR GB IT

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(30) Priority: 12.01.1995 US 371722

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(54) Synthetic power transmission fluids having enhanced performance capabilities

(57) A power transmission fluid composition which has, on a weight basis, an oil-soluble boron content of 0.001 to 0.1%, an oil-soluble phosphorus content of 0.005 to 0.2% and an oil-soluble metal content as metal-containing additive of no more than about 100 ppm and which comprises the following components:

matic viscosity at 100°C of at least  $5.0 \times 10^{-6}$  m<sup>2</sup>/s (5.0 cSt) after 20 hours in the Volkswagen taper roller bearing shear stability test.

a) at least about 70 wt% based on the total weight of the composition of an hydrogenated poly- $\alpha$ -olefin oligomer fluid having a kinematic viscosity of  $2 \times 10^{-6}$  to  $6 \times 10^{-6}$  m<sup>2</sup>/s (2 to 6 cSt) at 100°C;

b) on an active ingredient basis, 2 to 20 wt% based on the total weight of the composition of an acrylic viscosity index improver which is in the form of a solution with an inert solvent;

c) 4 to 25 wt% based on the total weight of the composition of an oil-soluble dialkyl ester of a C<sub>4</sub> to C<sub>14</sub>  $\alpha,\omega$ -dicarboxylic acid having a pour point of -45°C or lower;

d) a dispersant amount of an oil-soluble ashless dispersant;

e) a friction modifying amount an oil-soluble friction modifier; and

f) an oil-soluble inhibitor selected from foam inhibitors, copper corrosion inhibitors, rust inhibitors and oxidation inhibitors;

with the proviso that the power transmission fluid composition has (i) a kinematic viscosity of at least  $6.8 \times 10^{-6}$  m<sup>2</sup>/s (6.8 cSt) at 100°C, (ii) a Brookfield viscosity of 15 Pas (15,000 cP) or less at -40°C, (iii) a kinematic viscosity at 100°C of at least  $6.0 \times 10^{-6}$  m<sup>2</sup>/s (6.0 cSt) after 4 hours in the Volkswagen taper roller bearing shear stability test, and (iv) a kine-

## Description

TECHNICAL FIELD

This invention relates to oil-based power transmission fluid compositions, especially automatic transmission fluids, of enhanced performance capabilities.

BACKGROUND

The continuing development of new power transmission equipment gives rise to demands for new automatic transmission fluids capable of meeting increasingly severe performance requirements sought by the original equipment manufacturers and marketers of power transmission fluids. Among significant improvements in this regard are the ashless or low-ash synthetic base compositions described in U.S. Pat. Nos. 5,089,156 and 5,360,562 to D. R. Chrisope and R. J. Hartley. Those compositions, which utilize among other things mixtures of certain high and low viscosity hydrogenated poly- $\alpha$ -olefin oligomers and little or no high molecular weight viscosity index improvers, have excellent high and low temperature viscosity properties and excellent shear stability. Nevertheless, further progress in the field requires compositions which not only possess these properties, but which in addition exhibit superior seal performance and superior friction properties.

SUMMARY OF THE INVENTION

It has been found possible to fulfill the foregoing need while at the same time providing automatic transmission fluids that are advantageous from the environmental and economic standpoints. Pursuant to this invention fluids are provided which have little or no content of metals, and the small amount of metal if present is typically an innocuous metal such as calcium. At the same time it has been found possible to achieve substantial improvements in seal and friction performance through use of a synthetic base oil of relatively low viscosity provided such base such is suitably combined with particular additive components hereinafter described.

In accordance with this invention there is provided a power transmission fluid (ATF) composition wherein the composition has on a weight basis an oil-soluble boron content of about 0.001 to about 0.1%, an oil-soluble phosphorus content of about 0.005 to about 0.2%, and either no metal additive content or an oil-soluble metal content as one or more metal-containing additives of no more than about 100 ppm; wherein said composition comprises the following components:

- a) at least about 70 wt% based on the total weight of said composition of one or more hydrogenated poly- $\alpha$ -olefin oligomer fluids, this component having a viscosity in the range of about 2 to about 6 cSt at 100°C;
- b) on an active ingredient basis, about 2 to about 20 wt% based on the total weight of said composition of an acrylic viscosity index improver in the form of a solution in an inert solvent;
- c) about 4 to about 25 wt% based on the total weight of said composition of at least one oil-soluble dialkyl ester of a  $C_4$  to  $C_{14}$   $\alpha,\omega$ -dicarboxylic acid having a pour point of -45°C or lower;
- d) a dispersant amount of at least one oil-soluble ashless dispersant;
- e) a friction modifying amount of at least one oil-soluble friction modifier; and
- f) oil-soluble inhibitors selected from the group consisting of foam inhibitors, copper corrosion inhibitors, rust inhibitors, and oxidation inhibitors.

In addition, the components referred to above are selected and combined such that finished composition has (i) a kinematic viscosity of at least 6.8 cSt at 100°C, (ii) a Brookfield viscosity of 15,000 cP or less at -40°C, (iii) a kinematic viscosity at 100°C of at least 6.0 cSt after 4 hours in the Volkswagen taper roller bearing shear stability test, and (iv) a kinematic viscosity at 100°C of at least 5.0 cSt after 20 hours in the Volkswagen taper roller bearing shear stability test.

BRIEF DESCRIPTION OF THE DRAWINGS

Figures 1 through 6 are plots of data obtained on subjecting two different ATF compositions of this invention to the 3T40 band clutch friction test procedure of General Motors Corporation.

FURTHER DESCRIPTION OF THE INVENTION

Although the fluid compositions of this invention contain on a weight basis from none to no more than about 100 ppm (parts per million) of metals, these compositions do contain one or more components containing boron or phos-

phorus or a combination of boron and phosphorus, which elements of course are not classified as metals. Likewise small amounts of silicon in the form of silicone foam inhibitor may be, and preferably are, present in the compositions.

Among the features of this invention is the discovery that the type of hydrogenated poly- $\alpha$ -olefin oligomer fluid used can have a profound influence on the seal performance of the finished automatic transmission fluid. In particular, hydrogenated poly- $\alpha$ -olefin oligomer fluids having 100°C kinematic viscosities of 8, 10, 40 and 100 cSt tend to cause seal shrinking, especially in the case of ethylene-acrylic seal material and silicone seal material. In sharp contrast, the hydrogenated poly- $\alpha$ -olefin oligomer fluids used in the practice of this invention -- viz., one or more hydrogenated poly- $\alpha$ -olefin oligomer fluids as a fluid having a 100°C kinematic viscosity in the range of about 2 to about 6 cSt -- do not exert this deleterious effect. In fact, use of these less viscous hydrogenated poly- $\alpha$ -olefin oligomer fluids makes it possible to provide finished automatic fluid compositions which can pass all of the seal tests set forth in the current DEXRON® III specifications of General Motors Corporation and all of the seal tests set forth in the current MERCON® specifications of Ford Motor Company, which compositions constitute preferred embodiments of this invention. The DEXRON® III specifications of General Motors Corporation referred to herein are as published in GM-6297M, dated April 1993, and the MERCON® specifications of Ford Motor Company referred to herein are as revised in February 1993.

Moreover, this invention makes possible the provision of power transmission fluid compositions having an excellent combination of properties including excellent low temperature and high temperature viscosity properties, high shear stability, excellent thermal and oxidative stability, excellent friction properties, highly effective antiwear and extreme pressure properties, and good additive compatibility. This is made possible in part because of the beneficial mutual co-action among the principal components used in formulating the compositions of this invention. For example, the unification of the herein-described components a), b) and c) in the proportions set forth above makes it possible to achieve the vitally important high and low temperature viscosity properties, the shear stability properties, and the seal compatibility properties. The other components contribute to other advantageous properties, and at the same time do not materially detract from the excellent overall performance capabilities of the compositions.

It is important to note that prior general purpose lubricant compositions, crankcase lubricant compositions, gear lubricant compositions, metal working fluid compositions, cutting oil fluid compositions, slideway lubricant compositions, manual transmission fluid compositions, transformer oil compositions, hydraulic fluids, etc., cannot be used in the practice of this invention. The performance parameters which must be achieved and that have been achieved pursuant to this invention cannot be realized by any such compositions that have been designed, used or suggested for use for such other purposes. The present invention involves highly specialized automatic transmission fluid compositions, an area which is generally regarded in the art as constituting perhaps the most complex area of technology in the entire field of lubrication and power transmission fluids. The compositions of this invention are thus of greatest utility and are especially adapted for use as automatic transmission fluids, including use with the new generations of automatic transmissions equipped with electronically controlled torque converter clutches capable of operating in a continuous slip mode. The compositions of this invention can also be used as hydraulic fluids, although all of the excellent performance capabilities of the present compositions are unnecessary for such usage.

Preferably, the ashless dispersant used in the compositions of this invention is a phosphorus-containing dispersant, and more preferably, a boron- and phosphorus-containing dispersant. In one embodiment the entire phosphorus and boron content of the finished fluid is supplied by a boron- and phosphorus-containing dispersant, such as a boron- and phosphorus-containing succinimide dispersant, a boron- and phosphorus-containing Mannich base dispersant, or the like. In another embodiment the entire boron content of the finished fluid is supplied by a boron- and phosphorus-containing dispersant whereas the phosphorus content is supplied in part by the boron- and phosphorus-containing dispersant and in part by a non-dispersant metal-free oil-soluble nitrogen- and phosphorus-containing antiwear/extreme pressure agent such as an amine phosphate, or the like. In this latter embodiment it is especially preferred to proportion these components such that a major amount of the phosphorus content in the finished fluid is supplied by the dispersant and a minor amount is supplied by the non-dispersant antiwear/extreme pressure agent.

The finished compositions preferably contain a combination of all of the inhibitors referred to above. Thus the preferred compositions contain at least one foam inhibitor, at least one copper corrosion inhibitor, at least one rust inhibitor, and at least one oxidation inhibitor. Each such inhibitor type, whether comprised of one or more individual component materials of that type, is present in an amount that is at least sufficient to provide the functional performance for which it has been selected. Thus in accordance with this preferred embodiment, the finished fluid will contain a foam-inhibiting amount of one or more foam inhibitors, a copper corrosion-inhibiting amount of one or more copper corrosion inhibitors, a rust-inhibiting amount of one or more rust inhibitors, and an oxidation-inhibiting amount of one or more oxidation inhibitors. In selecting these components it is important to ensure that the components are mutually compatible with each other, and that none of them significantly detracts from or interferes with the performance capabilities of the overall finished fluid composition.

In this connection, while other inhibitor components can be used, preferred compositions are those in which the oil-soluble inhibitors include at least one thiadiazole such as a 2-mercapto-5-alkylthio-1,3,5-thiadiazole or 2,5-bis(alkylthio)-1,3,5-thiadiazole, at least one ring-alkylated diphenylamine, at least one sterically-hindered tertiary butyl

phenol, at least one calcium sulfurized alkylphenate, at least one alkoxypropylamine, at least one aliphatic monocarboxylic acid, at least one alkyl glycol nonionic surfactant, and silicone foam inhibitor.

Still another feature of this invention is the discovery that the compositions of this invention should be devoid of sulfurized esters and sulfurized olefinic compounds. Elimination of such commonly used materials has been found to materially increase the thermal and oxidative stability of the overall composition. In a preferred embodiment of this invention, the only sulfur-containing additive components present are (i) 100 ppm or less (preferably 50 ppm or less) of alkaline earth metal such as calcium added as an alkaline earth metal sulfurized alkylphenate or alkaline earth metal alkylbenzene sulfonate, and/or (ii) a thiadiazole copper corrosion inhibitor, such as an oil-soluble 2-mercapto-5-alkyldithio-1,3,5-thiadiazole and/or an oil-soluble 2,5-bis(alkyldithio)-1,3,5-thiadiazole. To illustrate the foregoing, an ATF fluid composition of this invention containing both (i) and (ii) but devoid of any sulfurized ester or sulfurized olefinic compound not will give passing results in the standard THOT test but will yield almost pristine transmission parts at the end of the test.

The compositions of this invention preferably include as friction modifier at least one N-aliphatic hydrocarbyl-substituted diethanol amine in which the N-aliphatic hydrocarbyl-substituent is at least one straight chain aliphatic hydrocarbyl group free of acetylenic unsaturation and having in the range of 14 to 20 carbon atoms. Other preferred friction modifiers which can be used include at least one N-aliphatic hydrocarbyl-substituted trimethylenediamine in which the N-aliphatic hydrocarbyl group is at least one straight chain aliphatic hydrocarbyl group free of acetylenic unsaturation and having in the range of about 14 to about 20 carbon atoms, or at least one hydroxyalkyl aliphatic imidazoline in which the hydroxyalkyl group contains from 2 to about 4 carbon atoms, and in which the aliphatic group is an acyclic hydrocarbyl group containing from about 10 to about 25 carbon atoms.

These and other embodiments and features of this invention will become still further apparent from the ensuing description and appended claims.

#### Component a)

As noted above, a major amount of the oleaginous liquids of this invention is compounded from one or more hydrogenated poly- $\alpha$ -olefin oligomer fluids. Such fluids are formed by oligomerization of 1-alkene hydrocarbon having 6 to 20 and preferably 8 to 16 carbon atoms in the molecule and hydrogenation of the resultant oligomer. Hydrogenated oligomers formed from 1-decene are particularly preferred. Commercially available products are usually composed of mixtures of individual oligomer species such as for example dimer, trimer and tetramer species. It is to be understood that the term "oligomer" does not place a limitation on the actual number of monomer units in the molecule, other than to distinguish the material from a higher polymer oil such as polyisobutene oil,

In general however the hydrogenated poly- $\alpha$ -olefin oligomer fluids in the viscosity range of 2 to 6 cSt at 100°C will usually not contain on a weight basis more than minor amounts (i.e., less than 50 wt%), if any, of species above hexamer.

Component a) whether a single species or a mixture of oligomeric species has a viscosity at 100°C in the range of about 2 to about 6 cSt. Thus commercially available hydrogenated poly- $\alpha$ -olefin oligomer fluids sold as 40 cSt or 100 cSt hydrogenated poly- $\alpha$ -olefin oligomer fluid mixtures are not used in the practice of this invention.

Most preferably component a) is composed of either (i) a single hydrogenated poly- $\alpha$ -olefin oligomer fluid or (ii) a mixture of at least two different hydrogenated poly- $\alpha$ -olefin oligomer fluids, wherein the single fluid of (i) or the resultant mixture of (ii) has a kinematic viscosity at 100°C in the range of about 4 to about 6 cSt, and better yet, a kinematic viscosity at 100°C in the range of about 4.5 to about 5.5 cSt.

Methods for the production of such liquid oligomeric 1-alkene hydrocarbons are known and reported in the literature. See for example U. S. Pat. Nos. 3,763,244; 3,780,128; 4,172,855; 4,218,330; and 4,950,822. Additionally, hydrogenated 1-alkene oligomers of this type and of suitable viscosity grades are available as articles of commerce, for example, under the DURASYN trademark from Albemarle Corporation. Suitable 1-alkene oligomers are also available from other suppliers.

Tabulated below are data concerning typical composition and properties of products of this type made from 1-decene. In these tabulations the typical compositions are expressed in terms of normalized area percentages by GC and "n.d." means "not determined".

#### 2 Centistoke poly- $\alpha$ -olefin oil:

Composition - Monomer 0.4, Dimer 90.7, Trimer 8.3, Tetramer 0.6.

Properties - Viscosity at 100°C: 1.80 cSt; Viscosity at 40°C: 5.54 cSt; Viscosity at -18°C: n.d.; Viscosity at -40°C: 306 cSt; Pour point: -63°C; Flash point (ASTM D 92): 165°C; NOACK volatility: 99%.

4 Centistoke poly- $\alpha$ -olefin oil:Composition - Trimer 82.7, Tetramer 14.6, Pentamer 2.7.Properties - Viscosity at 100°C: 4.06 cSt; Viscosity at 40°C: 17.4 cSt; Viscosity at -18°C: n.d.; Viscosity at -40°C: 2490 cSt; Pour point: <-65°C; Flash point (ASTM D 92): 224°C; NOACK volatility: 12.9%.6 Centistoke poly- $\alpha$ -olefin oil:Composition - Trimer 32.0, Tetramer 43.4, Pentamer 21.6, Hexamer 3.0.Properties - Viscosity at 100°C: 5.91 cSt; Viscosity at 40°C: 31.4 cSt; Viscosity at -18°C: n.d.; Viscosity at -40°C: 7877 cSt; Pour point: -63°C; Flash point (ASTM D 92): 235°C; NOACK volatility: 7.5%.75/25 Blend of 2 Centistoke and 4 Centistoke poly- $\alpha$ -olefin oils:Composition - Monomer 0.3, Dimer 66.8, Trimer 27.3, Tetramer 4.8, Pentamer 0.8.Properties - Viscosity at 100°C: 2.19 cSt; Viscosity at 40°C: 7.05 cSt; Viscosity at -18°C: 84.4 cSt; Viscosity at -40°C: 464 cSt; Pour point: <-65°C; Flash point (ASTM D 92): 166°C; NOACK volatility: 78.2%.50/50 Blend of 2 Centistoke and 4 Centistoke poly- $\alpha$ -olefin oils:Composition - Monomer 0.2, Dimer 44.7, Trimer 45.9, Tetramer 7.6, Pentamer 1.3, Hexamer 0.3.Properties - Viscosity at 100°C: 2.59 cSt; Viscosity at 40°C: 9.36 cSt; Viscosity at -18°C: 133 cSt; Viscosity at -40°C: 792 cSt; Pour point: <-65°C; Flash point (ASTM D 92): 168°C; NOACK volatility: 57.4%.25/75 Blend of 2 Centistoke and 4 Centistoke poly- $\alpha$ -olefin oils:Composition - Monomer 0.1, Dimer 23.1, Trimer 62.7, Tetramer 11.5, Pentamer 2.1, Hexamer 0.5.Properties - Viscosity at 100°C: 3.23 cSt; Viscosity at 40°C: 12.6 cSt; Viscosity at -18°C: 214 cSt; Viscosity at -40°C: 1410 cSt; Pour point: <-65°C; Flash point (ASTM D 92): 190°C; NOACK volatility: 30.8%.95/05 Blend of 4 Centistoke and 6 Centistoke poly- $\alpha$ -olefin oils:Composition - Dimer 0.5, Trimer 78.4, Tetramer 15.6, Pentamer 3.7, Hexamer 1.8.Properties - Viscosity at 100°C: 4.15 cSt; Viscosity at 40°C: 17.9 cSt; Viscosity at -18°C: n.d.; Viscosity at -40°C: 2760 cSt; Pour point: <-65°C; Flash point (ASTM D 92): 225°C; NOACK volatility: 10.5%.90/10 Blend of 4 Centistoke and 6 Centistoke poly- $\alpha$ -olefin oils:Composition - Dimer 0.3, Trimer 76.0, Tetramer 17.0, Pentamer 4.7, Hexamer 2.0.Properties - Viscosity at 100°C: 4.23 cSt; Viscosity at 40°C: 18.4 cSt; Viscosity at -18°C: n.d.; Viscosity at -40°C: 2980 cSt; Pour point: <-65°C; Flash point (ASTM D 92): 228°C; NOACK volatility: 11.4%.80/20 Blend of 4 Centistoke and 6 Centistoke poly- $\alpha$ -olefin oils:Composition - Dimer 0.3, Trimer 71.5, Tetramer 19.4, Pentamer 6.5, Hexamer 2.3.Properties - Viscosity at 100°C: 4.39 cSt; Viscosity at 40°C: 19.9 cSt; Viscosity at -18°C: n.d.; Viscosity at -40°C: 3240 cSt; Pour point: <-65°C; Flash point (ASTM D 92): 227°C; NOACK volatility: 9.2%.75/25 Blend of 4 Centistoke and 6 Centistoke poly- $\alpha$ -olefin oils:Composition - Dimer 0.7, Trimer 69.0, Tetramer 21.0, Pentamer 7.3, Hexamer 2.0.Properties - Viscosity at 100°C: 4.39 cSt; Viscosity at 40°C: 20.1 cSt; Viscosity at -18°C: 436 cSt; Viscosity at -40°C: 3380 cSt; Pour point: <-65°C; Flash point (ASTM D 92): 226°C; NOACK volatility: 14.2%.50/50 Blend of 4 Centistoke and 6 Centistoke poly- $\alpha$ -olefin oils:Composition - Dimer 0.4, Trimer 57.3, Tetramer 27.4, Pentamer 11.8, Hexamer 3.1.Properties - Viscosity at 100°C: 4.82 cSt; Viscosity at 40°C: 23.0 cSt; Viscosity at -18°C: 544 cSt; Viscosity at -40°C: 4490 cSt; Pour point: <-65°C; Flash point (ASTM D 92): 226°C; NOACK volatility: 12.5%.

25/75 Blend of 4 Centistoke and 6 Centistoke poly- $\alpha$ -olefin oils:

Composition - Dimer 0.3, Trimer 45.3, Tetramer 33.4, Pentamer 16.4, Hexamer 4.6.

Properties - Viscosity at 100°C: 5.38 cSt; Viscosity at 40°C: 26.8 cSt; Viscosity at -18°C: 690 cSt; Viscosity at -40°C: 6020 cSt; Pour point: <-65°C; Flash point (ASTM D 92): 250°C; NDACK volatility: 9.2%.

Hydrogenated oligomers of this type contain little, if any, residual ethylenic unsaturation. Preferred oligomers are formed by use of a Friedel-Crafts catalyst (especially boron trifluoride promoted with water or a  $C_{1-20}$  alkane) followed by catalytic hydrogenation of the oligomer so formed using procedures such as are described in the foregoing U.S. patents.

Other catalyst systems which can be used to form oligomers of 1-alkene hydrocarbons, which, on hydrogenation, provide suitable oleaginous liquids include Ziegler catalysts such as ethyl aluminum sesquichloride with titanium tetrachloride, aluminum alkyl catalysts, chromium oxide catalysts on silica or alumina supports and a system in which a boron trifluoride catalyst oligomerization is followed by treatment with an organic peroxide.

Component b)

This component is an acrylic viscosity index improver which is supplied in the form of an solution in an inert solvent, typically a mineral oil solvent, which usually is a severely refined mineral oil. The viscosity index improver solution as received often will have a boiling point above 200°C, and a specific gravity of less than 1 at 25°C. In addition, it has sufficient shear stability such that the finished composition has a kinematic viscosity at 100°C of at least 6.0 cSt after 4 hours in the Volkswagen taper roller bearing shear stability test, and a kinematic viscosity at 100°C of at least 5.0 cSt after 20 hours in the Volkswagen taper roller bearing shear stability test. Preferably, the acrylic viscosity index improver has sufficient shear stability to enable the finished composition to possess a viscosity of at least 6.8 cSt at 100°C after 40 cycles in the FISST (Fuel Injector Shear Stability Test) of ASTM D-5275, formerly known as the ASTM D-3945b method. On an active ingredient basis (i.e., excluding the weight of inert diluent or solvent associated with the viscosity index improver as supplied), the finished fluid compositions of this invention will normally contain in the range of about 2 to about 20 wt% of the polymeric viscosity index improver. Small departures from this range may be resorted to as necessary or desirable in any given situation.

Suitable proprietary materials for use as component b) are available from RÖHM GmbH (Darmstadt, Germany) under the trade designations: VISCOPLEX® 5543, VISCOPLEX® 5548, VISCOPLEX® 5549, VISCOPLEX® 5550, VISCOPLEX® 5551 and VISCOPLEX® 5151, and from Rohm & Haas Company (Philadelphia, Pennsylvania) under the trade designations ACRYLOID® 1277 and ACRYLOID® 1265E. Mixtures of the foregoing products can also be used. It is possible that other manufacturers may also have viscosity index improvers having the requisite performance properties required for use as component b). Details concerning the chemical composition and methods for the manufacture of such products are maintained as trade secrets by manufacturers of such products.

Preferably, the acrylic viscosity index will be provided as a hydrocarbon solution having a polymer content in the range of from about 50 to about 75 wt% and a nitrogen content in the range of about 0.15 to about 0.25 wt%. Such products preferably exhibit a permanent shear stability index (a PSSI value) using ASTM test method D-3945a of no higher than about 35, preferably 30 or less, and most preferably 15 or less.

Component c)

This component serves in a number of capacities. Besides being a minor but important component of the base oil itself, component c) functions as a seal swell agent and as a solubilizing/compatibilizing agent, and thus plays important roles in the compositions of this invention. As noted above, component c) is one or more oil-soluble dialkyl esters of a  $C_4$  to  $C_{14}$  (preferably  $C_6$  to  $C_{10}$ )  $\alpha,\omega$ -dicarboxylic acid having a pour point of -45°C or lower, and preferably a pour point of -55°C or lower. Examples of such materials include diisodecyl glutarate, diisododecyl glutarate, diisooctyl adipate, di(2-ethylhexyl) adipate, diisononyl adipate, diisododecyl adipate, di(tridecyl) adipate, di(2-ethylhexyl) sebacate, diisooctyl sebacate, dioctyl azelate, diisooctyl azelate, di(2-ethylhexyl) azelate, diisooctyl dodecanedioate, and mixtures thereof. Generally speaking, the most suitable diesters include the adipates, azelates, and sebacates of  $C_8$ - $C_{13}$  alkanols (or mixtures thereof). Mixtures of two or more different types of diesters (e.g., dialkyl adipates and dialkyl azelates, etc.) can also be used. Most preferred are the oil-soluble dialkyl esters of adipic acid having a pour point of -55°C or lower.

As noted above, component c) is normally present at a concentration in the range of about 4 to about 25 wt% based on the total weight of the finished power transmission fluid composition. Generally speaking, the higher the molecular weight of the ester, the higher should be the treat rate within the foregoing range. Small departures from this range may be made whenever deemed necessary or desirable.

Component d)

The ashless dispersant can be of various types including succinimides, succinamides, succinic ester-amides, Mannich products, long chain hydrocarbyl amines, polyol esters, or the like. Of these, the succinimides are preferred for use in the practice of this invention.

Methods for the production of the foregoing types of ashless dispersants are known to those skilled in the art and are reported in the patent literature. For example, the synthesis of various ashless dispersants of the foregoing types is described in such patents as U.S. 2,459,112; 2,962,442; 2,984,550; 3,036,003; 3,163,603; 3,166,516; 3,172,892; 3,184,474; 3,202,678; 3,215,707; 3,216,936; 3,219,666; 3,236,770; 3,254,025; 3,271,310; 3,272,746; 3,275,554; 3,281,357; 3,306,908; 3,311,558; 3,316,177; 3,331,776; 3,340,281; 3,341,542; 3,346,493; 3,351,552; 3,355,270; 3,368,972; 3,381,022; 3,399,141; 3,413,347; 3,415,750; 3,433,744; 3,438,757; 3,442,808; 3,444,170; 3,448,047; 3,448,048; 3,448,049; 3,451,933; 3,454,497; 3,454,555; 3,454,607; 3,459,661; 3,461,172; 3,467,668; 3,493,520; 3,501,405; 3,522,179; 3,539,633; 3,541,012; 3,542,680; 3,543,678; 3,558,743; 3,565,804; 3,567,637; 3,574,101; 3,576,743; 3,586,629; 3,591,598; 3,600,372; 3,630,904; 3,632,510; 3,632,511; 3,634,515; 3,649,229; 3,697,428; 3,697,574; 3,703,536; 3,704,308; 3,725,277; 3,725,441; 3,725,480; 3,726,882; 3,736,357; 3,751,365; 3,756,953; 3,793,202; 3,798,165; 3,798,247; 3,803,039; 3,804,763; 3,836,471; 3,862,981; 3,936,480; 3,948,800; 3,950,341; 3,957,854; 3,957,855; 3,980,569; 3,991,098; 4,071,548; 4,173,540; 4,234,435; 5,137,980 and Re 26,433.

As used herein the term "ashless dispersant" means that the dispersant does not contain any metal constituent. As made clear above, the dispersant may contain boron, and preferably contains phosphorus, and most preferably contains both boron and phosphorus, elements which of course are not metals. Thus the term "ashless dispersant" encompasses dispersants which contain either or both of boron and phosphorus, even though such dispersant when thermally decomposed may leave some residues containing boron or phosphorus, or both.

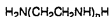
The preferred ashless dispersants are one or more alkenyl succinimides of an amine having at least one primary amino group capable of forming an imide group. The alkenyl succinimides may be formed by conventional methods such as by heating an alkenyl succinic anhydride, acid, acid-ester, acid halide, or lower alkyl ester with an amine containing at least one primary amino group. The alkenyl succinic anhydride may be made readily by heating a mixture of polyolefin and maleic anhydride to about 180°-220°C. The polyolefin is preferably a polymer or copolymer of a lower monoolefin such as ethylene, propylene, isobutene and the like, having a number average molecular weight in the range of about 700 to about 2100 as determined by gel permeation chromatography (GPC). The more preferred source of alkenyl group is from polyisobutene having a GPC molecular weight in the range of about 800 to about 1800. In a still more preferred embodiment the alkenyl group is a polyisobutenyl group derived from polyisobutene having a GPC number average molecular weight of about 800-1350, and most preferably in the range of about 900-1100.

Mannich base dispersants are also a highly useful type of ashless dispersant for use in the practice of this invention.

Amines which may be employed in forming the ashless dispersant include any that have at least one primary amino group which can react to form an imide group and at least one additional primary or secondary amino group and/or at least one hydroxyl group. A few representative examples are: N-methyl-propanediamine, N-dodecyl-propanediamine, N-aminopropyl-piperazine, ethanolamine, N-ethanol-ethylenediamine and the like.

Preferred amines are the alkylene polyamines, such as propylene diamine, dipropylene triamine, di-(1,2-butylene)triamine, and tetra-(1,2-propylene)pentamine.

The most preferred amines are the ethylene polyamines which can be depicted by the formula



wherein n is an integer from one to about ten. These include: ethylene diamine, diethylene triamine, triethylene tetramine, tetraethylene pentamine, pentaethylene hexamine, and the like, including mixtures thereof in which case n is the average value of the mixture. These depicted ethylene polyamines have a primary amine group at each end so can form mono-alkenylsuccinimides and bis-alkenylsuccinimides. Commercially available ethylene polyamine mixtures usually contain minor amounts of branched species and cyclic species such as N-aminoethyl piperazine, N,N'-bis(aminooethyl)piperazine, N,N'-bis(piperazinyl)ethane, and like compounds. The preferred commercial mixtures have approximate overall compositions falling in the range corresponding to diethylene triamine to tetraethylene pentamine, mixtures generally corresponding in overall makeup to tetraethylene pentamine being most preferred.

Especially preferred ashless dispersants for use in the present invention are the products of reaction of a polyethylene polyamine, e.g. triethylene tetramine or tetraethylene pentamine, with a hydrocarbon substituted carboxylic acid or anhydride made by reaction of a polyolefin, preferably polyisobutene, of suitable molecular weight, with an unsaturated polycarboxylic acid or anhydride, e.g., maleic anhydride, maleic acid, fumaric acid, or the like, including mixtures of two or more such substances.

When the ashless dispersant contains phosphorus, it serves as a multipurpose component in that it is an anti-wear/extreme pressure agent as well as a dispersant. Accordingly, when a phosphorus-containing or boron- and phosphorus-

phorus-containing dispersant is used it can supply all or a portion of the requisite phosphorus content of the finished fluid composition.

Methods suitable for introducing phosphorus or boron or a combination of phosphorus and boron into ashless dispersants are known and reported in the patent literature. One may refer, for example, to such U.S. patents as 3,087,936; 3,184,411; 3,185,645; 3,235,497; 3,254,025, 3,265,618; 3,281,428; 3,282,955; 3,284,410; 3,324,032; 3,338,832; 3,344,069; 3,403,102; 3,428,561; 3,502,677; 3,511,780; 3,513,093; 3,533,945; 3,623,985; 3,718,663; 3,865,740; 3,945,933; 3,950,341; 3,991,056; 4,093,614; 4,097,389; 4,428,849; 4,338,205; 4,428,849; 4,554,086; 4,615,826; 4,634,543; 4,648,980; 4,747,971, and 4,857,214. The procedures that are described in U.S. 4,857,214 are especially preferred for use in forming component e) of the compositions of this invention.

Accordingly, one preferred group of phosphorus- and/or boron-containing ashless dispersants comprises aliphatic hydrocarbyl-substituted succinimide of a mixture of cyclic and acyclic polyethylene polyamines having an approximate average overall composition falling in the range of from diethylene triamine through pentaethylene hexamine, said succinimide being heated with (1) at least one phosphorylating agent to form a phosphorus-containing succinimide ashless dispersant; or (2) at least one boronating agent to form a boron-containing succinimide ashless dispersant; or (3) either concurrently or in any sequence with at least one phosphorylating agent and at least one boronating agent to form a phosphorus- and boron-containing succinimide ashless dispersant. Particularly preferred ashless dispersants for use as component e) are aliphatic hydrocarbyl-substituted succinimides of the type described above which have been heated concurrently or in any sequence with a boron compound such as a boron acid, boron ester, boron oxide, or the like (preferably boric acid) and one or more inorganic phosphorus compounds such as an acid or anhydride (preferably phosphorous acid,  $H_3PO_3$ ) or a partial or total sulfur analog thereof to form an oil-soluble product containing both boron and phosphorus. The use of the partial or total sulfur analogs is less preferred.

The amount of ashless dispersant on an "as received basis" (i.e., including the weight of impurities, diluents and solvents typically associated therewith) is generally within the range of about 1 to about 15 wt%, typically within the range of about 1 to about 10 wt%, preferably within the range of about 1 to about 6 wt%, and most preferably within the range of about 2 to about 5 wt%.

#### Component e)

The compositions of this invention contain one or more friction modifiers. These include such compounds as aliphatic amines or ethoxylated aliphatic amines, aliphatic fatty acid amides, aliphatic carboxylic acids, aliphatic carboxylic esters, aliphatic carboxylic ester-amides, aliphatic phosphonates, aliphatic phosphates, aliphatic thiophosphonates, aliphatic thiophosphates, etc., wherein the aliphatic group usually contains above about eight carbon atoms so as to render the compound suitably oil soluble. Also suitable are aliphatic substituted succinimides formed by reacting one or more aliphatic succinic acids or anhydrides with ammonia.

One preferred group of friction modifiers is comprised of the N-aliphatic hydrocarbyl-substituted diethanol amines in which the N-aliphatic hydrocarbyl-substituent is at least one straight chain aliphatic hydrocarbyl group free of acetylenic unsaturation and having in the range of about 14 to about 20 carbon atoms.

A particularly preferred friction modifier system is composed of a combination of at least one N-aliphatic hydrocarbyl-substituted diethanol amine and at least one N-aliphatic hydrocarbyl-substituted trimethylene diamine in which the N-aliphatic hydrocarbyl-substituent is at least one straight chain aliphatic hydrocarbyl group free of acetylenic unsaturation and having in the range of about 14 to about 20 carbon atoms. Further details concerning this friction modifier system are set forth in U.S. Pat. Nos. 5,372,735 and 5,441,656 (both by Ontani et al.).

Another particularly preferred friction modifier system is based on the combination of (i) at least one di(hydroxyalkyl) aliphatic tertiary amine in which the hydroxyalkyl groups, being the same or different, each contain from 2 to about 4 carbon atoms, and in which the aliphatic group is an acyclic hydrocarbyl group containing from about 10 to about 25 carbon atoms, and (ii) at least one hydroxyalkyl aliphatic imidazoline in which the hydroxyalkyl group contains from 2 to about 4 carbon atoms, and in which the aliphatic group is an acyclic hydrocarbyl group containing from about 10 to about 25 carbon atoms. For further details concerning this friction modifier system, reference should be had to U.S. Pat. No. 5,344,579.

Generally speaking, the compositions of this invention will contain up to about 1.25 wt%, and preferably from about 0.05 to about 1 wt% of one or more friction modifiers.

#### Component f)

This component will normally comprise a plurality of inhibitor components serving different functions. The inhibitors may be introduced in a preformed additive package which may contain in addition one or more other components used in the compositions of this invention. Alternatively these inhibitor components can be introduced individually or in various sub-combinations. While amounts can be varied within reasonable limits, the finished fluids of this invention will typically have a total inhibitor content in the range of about 0.2 to about 2 wt% and preferably about 0.5 to about 1 wt%, both on



an "active ingredient" -- i.e., excluding the weight of inert materials such as solvents or diluents that may be associated therewith.

Foam inhibitors form one type inhibitor suitable for use as inhibitor components in the compositions of this invention. These include silicones, polyacrylates, surfactants, and the like. One suitable acrylic defoamer material is PC-1244 (Monsanto Company).

Copper corrosion inhibitors constitute another class of additives suitable for inclusion in the compositions of this invention. Such compounds include thiazoles, triazoles and thiadiazoles. Examples of such compounds include benzotriazole, tolyltriazole, octyltriazole, decyltriazole, dodecyltriazole, 2-mercapto benzothiazole, 2,5-dimercapto-1,3,4-thiadiazole, 2-mercapto-5-hydrocarbylthio-1,3,4-thiadiazoles, 2-mercapto-5-hydrocarbyldithio-1,3,4-thiadiazoles, 2,5-bis(hydrocarbylthio)-1,3,4-thiadiazoles, and 2,5-bis(hydrocarbyldithio)-1,3,4-thiadiazoles. The preferred compounds are the 1,3,4-thiadiazoles, a number of which are available as articles of commerce, and also combinations of triazoles such as tolyltriazole with a 1,3,5-thiadiazole such as a 2,5-bis(alkyldithio)-1,3,4-thiadiazole or 2-alkyldithio-5-mercapto-1,3,4-thiadiazole. Materials of these types that are available on the open market include Cobratelc TT-100 and HITEC® 4313 additive (Ethyl Petroleum Additives, Inc.). The 1,3,4-thiadiazoles are generally synthesized from hydrazine and carbon disulfide by known procedures. See, for example, U.S. Pat. Nos. 2,765,289; 2,749,311; 2,760,933; 2,850,453; 2,910,439; 3,663,561; 3,862,798; and 3,840,549.

Rust or corrosion inhibitors comprise another type of inhibitor additive for use in this invention. Such materials include monocarboxylic acids and polycarboxylic acids. Examples of suitable monocarboxylic acids are octanoic acid, decanoic acid and dodecanoic acid. Suitable polycarboxylic acids include dimer and trimer acids such as are produced from such acids as tall oil fatty acids, oleic acid, linoleic acid, or the like. Products of this type are currently available from various commercial sources, such as, for example, the dimer and trimer acids sold under the HYSTRENE trademark by the Humko Chemical Division of Witco Chemical Corporation and under the EMPOL trademark by Henkel Corporation. Another useful type of rust inhibitor for use in the practice of this invention is comprised of the alkenyl succinic acid and alkenyl succinic anhydride corrosion inhibitors such as, for example, tetrapropenylsuccinic acid, tetrapropenylsuccinic anhydride, tetradecenylsuccinic acid, tetradecenylsuccinic anhydride, hexadecenylsuccinic acid, hexadecenylsuccinic anhydride, and the like. Also useful are the half esters of alkenyl succinic acids having 8 to 24 carbon atoms in the alkenyl group with alcohols such as the polyglycols. Other suitable rust or corrosion inhibitors include ether amines; acid phosphates; amines; polyethoxylated compounds such as ethoxylated amines, ethoxylated phenols, and ethoxylated alcohols; imidazolines; aminosuccinic acids or derivatives thereof, and the like. Materials of these types are available as articles of commerce. Mixtures of such rust or corrosion inhibitors can be used.

Oxidation inhibitors constitute still another group of inhibitors which are preferably included in the compositions of this invention. These materials are exemplified by the phenolic antioxidants, aromatic amine antioxidants, sulfurized phenolic antioxidants, and organic phosphites, among others. Examples of phenolic antioxidants include 2,6-di-tert-butylphenol, liquid mixtures of tertiary butylated phenols, 2,6-di-tert-butyl-4-methylphenol, 4,4'-methylenebis(2,6-di-tert-butylphenol), 2,2'-methylenebis(4-methyl-6-tert-butylphenol), mixed methylene-bridged polyalkyl phenols, and 4,4'-thiobis(2-methyl-6-tert-butylphenol). N,N'-di-sec-butyl-p-phenylenediamine, 4-isopropylaminodiphenyl amine, phenyl- $\alpha$ -naphthyl amine, phenyl-p-naphthyl amine, and ring-alkylated diphenylamines serve as examples of aromatic amine antioxidants. Most preferred are the sterically hindered tertiary butylated phenols, the ring alkylated diphenylamines and combinations thereof.

The amounts of the inhibitor components used will depend to some extent upon the composition of the component and its effectiveness when used in the finished composition. However, generally speaking, the finished fluid will typically contain the following concentrations (weight percent) of the inhibitor components (active ingredient basis):

Inhibitor	Typical Range	Preferred Range
Foam inhibitor	0 to 0.1	0.01 to 0.08
Copper corrosion inhibitor	0 to 1.5	0.01 to 1
Rust inhibitor	0 to 0.5	0.01 to 0.3
Oxidation inhibitor	0 to 1	0.1 to 0.6

## Other Components

Very small amounts of certain metal-containing detergents such as calcium sulfurized phenates and calcium alkylbenzene sulfonate can also be used. However, as noted above, if an oil-soluble phenate or sulfonate is used it should be proportioned such that the finished fluid contains no more than about 100 ppm of metal, and preferably no more than about 50 ppm of metal. The sulfurized phenates are preferably neutral salts containing a stoichiometric amount of calcium, and in any event should have a total base number (TBN) of not more than about 200 mg KOH/gram.

In another preferred embodiment, the finished fluid will contain only two sulfur-containing additive components, namely, (i) one or more oil-soluble calcium sulfurized alkylphenates and (ii) one or more oil-soluble 1,3,5-thiadiazole copper corrosion inhibitors such as a 2,5-bis(alkyldithio)-1,3,5-thiadiazole. In other words, these preferred compositions are devoid of conventional sulfur-containing antiwear additives such as sulfurized olefins (sulfurized isobutylene, etc), dihydrocarbyl polysulfides, sulfurized fatty acids, and sulfurized fatty acid esters.

When the phosphorus content of the finished fluid is not completely supplied by use of a phosphorus-containing ashless dispersant (or a boron- and phosphorus-containing ashless dispersant), the remainder of the phosphorus content is preferably supplied by inclusion in the composition of one or more phosphorus-containing esters or acid-esters such as oil-soluble organic phosphites, oil-soluble organic acid phosphites, oil-soluble organic phosphates, oil-soluble organic acid phosphates, oil-soluble phosphoramidates, and oil-soluble phosphetanes. Examples include trihydrocarbyl phosphates, trihydrocarbyl phosphites, dihydrocarbyl phosphates, dihydrocarbyl phosphonates or dihydrocarbyl phosphites or mixtures thereof, monohydrocarbyl phosphates, monohydrocarbyl phosphites, and mixtures of any two or more of the foregoing. Oil-soluble amine salts of organic acid phosphates are a preferred category of auxiliary phosphorus-containing additives for use in the fluids of this invention. Sulfur-containing analogs of any of the foregoing compounds can also be used, but are less preferred. Most preferred as a commercially-available auxiliary phosphorus additive is an amine phosphate antiwear/extreme pressure agent; available from Ciba-Geigy Corporation as Irgalube 349.

Thus, in one of its embodiments, this invention provides compositions which contain a phosphorus-containing ashless dispersant such as a succinimide, a boron-containing ashless dispersant such as a succinimide, and/or a phosphorus- and boron-containing ashless dispersant such as a succinimide, together with at least one phosphorus-containing substance selected from (1) one or more inorganic acids of phosphorus; or (2) one or more inorganic thioacids of phosphorus; or (3) one or more monohydrocarbyl esters of one or more inorganic acids of phosphorus; or (4) one or more monohydrocarbyl esters of one or more inorganic thioacids of phosphorus; or (5) any combination of any two, or any three or all four of (1), (2), (3), and (4); or at least one oil-soluble amine salt or complex or adduct of any of (1), (2), (3), (4), and (5), said amine optionally being in whole or in part an amine moiety in (i) a basic nitrogen-containing ashless dispersant such as a succinimide or (ii) a boron- and basic nitrogen-containing ashless dispersant such as a succinimide or (iii) a phosphorus- and basic nitrogen-containing ashless dispersant such as a succinimide or (iv) a phosphorus-, boron- and basic nitrogen-containing ashless dispersant such as a succinimide.

The boron content of the compositions of this invention is preferably supplied by use of a boron-containing ashless dispersant or a boron- and phosphorus-containing ashless dispersant. When the boron content of the finished fluid is not completely supplied in this manner, the remainder of the boron content is preferably supplied by inclusion in the composition of one or more oil-soluble boron esters such as a glycol borate or glycol bborate.

Although not necessary, supplemental seal swell agents may be used. These include sulfone materials such as described in U.S. Pat. Nos. 3,974,081 and 4,029,587. Lubrizol 730 additive (The Lubrizol Corporation) is understood to be a commercially-available sulfone type seal swell agent. The phthalates of C<sub>4</sub>-C<sub>13</sub> alkanols (or mixtures thereof) are also potential supplemental seal swell additives. Other materials that may be considered for use include polyol esters such as Emery 2935, 2936, and 2939 esters from the Emery Group of Henkel Corporation and Hatcol 2352, 2962, 2925, 2938, 2939, 2970, 3178, and 4322 polyol esters from Hatco Corporation.

Dyes, pour point depressants, air release agents, and the like can also be included in the compositions of this invention.

In selecting any of the foregoing additives, it is important to ensure that each selected component is soluble in the fluid composition, is compatible with the other components of the composition, and does not interfere significantly with the requisite viscosity or shear stability properties of the overall finished fluid composition.

The individual components employed can be separately blended into the base fluid or can be blended therein in various subcombinations, if desired. Ordinarily, the particular sequence of such blending steps is not critical. Moreover, such components can be blended in the form of separate solutions in a diluent. It is preferable, however, to blend the additive components used in the form of an additive concentrate, as this simplifies the blending operations, reduces the likelihood of blending errors, and takes advantage of the compatibility and solubility characteristics afforded by the overall concentrate.

Additive concentrates can thus be formulated to contain all of the additive components and if desired, some of the base oil component a) and/or c), in amounts proportioned to yield finished fluid blends consistent with the concentrations described above. In most cases, the additive concentrate will contain one or more diluents such as light mineral

oils, to facilitate handling and blending of the concentrate. Thus concentrates containing up to about 50% by weight of one or more diluents or solvents can be used, provided the solvents are not present in amounts that interfere with the low and high temperature and flash point characteristics and the performance of the finished power transmission fluid composition. In this connection, the additive components utilized pursuant to this invention should be selected and proportioned such that an additive concentrate or package formulated from such components will have a flash point of 170°C or above, and preferably a flash point of at least 180°C, using the ASTM D-92 test procedure.

It is deemed possible, but not desirable, to utilize blends of components a) and b) with one or more other base oils having suitable viscosities, provided that the resultant blend contains a major proportion of the combination of components a), b), and c), and in addition possesses the requisite compatibility, viscosity properties, shear stability, and performance criteria (e.g., friction retention and durability, wear resistance, oxidation resistance and seal compatibility) for use in accordance with this invention.

Illustrative of such potentially useable auxiliary base oils and fluids of lubricating viscosity are hydrotreated mineral oils preferably in the range of about 55N to about 100N, and more preferably in the range of about 60N to about 80N, and most preferably the hydrotreated oils should be substantially wax-free. Likewise certain dewaxed highly paraffinic mineral oils having the requisite viscosity parameters and produced by processing other than hydrotreatment may be used in small amounts as auxiliary base oils. Synthetic esters such as mixed C<sub>9</sub> and C<sub>11</sub> dialkylphthalates (e.g., ICI Emkarete 911P ester oil), trimethylol propane trioleate, di-*isotridecyl* adipate (e.g., BASF Glissolfluid A13), pentaerythritol tetraheptanoate and equivalent synthetic base oils may be found suitable. However in all cases the overall base oil must contain at least about 70 wt% (and most preferably at least about 75 wt%) of component a).

The practice and advantages of this invention are illustrated by the following illustrative examples in which all values are percentages by weight on an "as received basis". In these Examples Component a) is composed of mixtures made from at least two of DURASYN 162 ("2 cSt"); DURASYN 164 ("4 cSt"); and DURASYN 166 ("6 cSt") poly- $\alpha$ -olefin oils (Albemarle Corporation) proportioned such that the mixture of the selected oils has a kinematic viscosity in the range of 2 to 6 cSt at 100°C. Component b) is either Viscoplex 5549 ("5549") or Viscoplex 5151 ("5151"). Component c) is diisooctyl adipate ("DIOA") which has a nominal pour point of approximately -68°C. Component d) is a boronated and phosphorylated preblend composition prepared substantially as described in Example 1A of U.S. Pat. No. 4,857,214, and the Silicone fluid is a 4% solution of poly(dimethylsiloxane) in light oil.

#### EXAMPLES 1-10

Automatic transmission fluids are formed by blending together the components in the proportions as specified in Tables 1 and 2.

Table 1

Components	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5
Component a) - 2 cSt	5.00	5.00	--	3.00	2.00
Component a) - 4 cSt	25.68	25.68	31.18	25.68	28.68
Component a) - 6 cSt	44.96	44.73	44.96	44.96	44.91
Component b) - 5549	5.50	5.50	5.00	5.50	5.50
Component b) - 5151	--	--	--	--	--
Component c) - DIOA	14.00	14.00	14.00	16.00	14.00
Component d)	3.77	4.00	3.77	3.77	3.77
Ethomeen T-12	0.10	0.10	0.12	0.10	0.12
Unamine O	--	--	--	--	0.01
Naugalube 438L	0.30	0.26	0.26	0.30	0.30
HITEC® 4735	0.20	0.20	0.20	0.20	0.20
HITEC® 314	0.04	0.04	0.04	0.04	0.04
PC-1244	0.03	0.03	0.03	0.03	0.03
Silicone fluid	0.02	0.02	0.02	0.02	0.02
OLOA 216C	0.05	0.04	0.05	0.05	0.05
Mazawet 77	0.05	0.04	0.05	0.05	0.05
Tomah PA14	0.05	0.05	0.05	0.05	0.05
Octanoic acid	0.05	0.05	0.05	0.05	0.05
Red Dye	0.02	0.02	0.02	0.02	0.02
Diluent oil - 45N	0.18	0.24	0.20	0.18	0.20

Table 2

Components	Ex 6	Ex 7	Ex 8	Ex 9	Ex 10
Component a) - 2 cSt	--	3.00	3.00	--	--
Component a) - 4 cSt	31 18	25.00	25.00	29.00	29.00
Component a) - 6 cSt	44 96	43.96	43.91	43.96	43.505
Component b) - 5549	5.00	--	--	--	--
Component b) - 5151	--	8 18	8.18	7 18	7.18
Component c) - DIOA	14 00	15.00	15.00	15.00	15.00
Component d)	3.77	3.77	3.77	3.77	4.00
Ethomeen T-12	0.10	0.12	0.12	0.12	0.10
Duomeen O	0.005	--	--	--	0.005
Unamine O	0.01	--	0 01	--	0.01
Naugalube 438L	0.26	0.26	0.26	0.26	0.30
HiTEC® 4735	0.20	0.20	0.20	0.20	0.25
HiTEC® 314	0.04	0.04	0.04	0.04	0.05
Irgalube 349	--	--	0 04	--	0.05
PC-1244	0.03	0.03	0.03	0.03	0.02
Silicone fluid	0.02	0.02	0.02	0.02	0.02
OLOA 216C	0.04	0.05	0.04	0.05	0.04
Mazawet 77	0.05	0.05	0.04	0.05	0.05
Tomah PA14	0.05	0.05	0.05	0.05	0.05
Octanoic acid	0.05	0.05	0.05	0.05	0.05
Red Dye	0.02	0.02	0.02	0.02	0.02
Diluent oil - 45N	0.215	0.20	0.22	0.20	0.30

Although each of the above compositions has not been evaluated, all experimental results obtained to date indicate that the compositions of the foregoing examples will possess (i) a kinematic viscosity of at least 6.8 cSt at 100°C, (ii) a Brookfield viscosity of 15,000 cP or less at -40°C, (iii) a kinematic viscosity at 100°C of at least 6.0 cSt after 4 hours in the Volkswagen taper roller bearing shear stability test, and (iv) a kinematic viscosity at 100°C of at least 5.0 cSt after 20 hours in the Volkswagen taper roller bearing shear stability test. In addition, evaluations to date indicate that the compositions possess an excellent combination of performance properties deemed necessary to satisfy the requirements for a premium grade automatic transmission fluid.

For example, Figs. 1-3 are plots of friction properties of a ATF of this invention as determined by use of the Standard 3T40 Band Friction Test of General Motors Corporation. Fig. 1 shows the engagement times in seconds as measured throughout the test. It will be seen that not only did these engagement times remain within the prescribed specification limits of 0.35 second minimum and 0.55 second maximum, but in addition the values were on the low side of this range. This is very desirable as it translates into higher mid-point dynamic torque as is shown by the results plotted in Fig. 2 which remained within the prescribed specification limits of 185 to 230 Newton-meters (Nm). The end torque values also expressed in Newton-meters shown in Fig. 3 likewise are very desirable as they remained well above the prescribed minimum specification value of 170 Nm throughout the test. The corresponding results shown in Figs. 4-6 obtained with another fluid of this invention show the same excellent friction performance in the same test procedure.

The excellent seal compatibility performance made possible from the practice of this invention is illustrated by the data set forth in Tables 3-6. Tables 3 and 4 show the performance of two fluids of this invention in the current Dexron® III test procedure. Their performance in the Mercon® test procedure is shown in Tables 5 and 6, in all cases passing results were achieved.

Table 3

Seal Material	Property	Results	Test Limits
Polyacrylic (A)	Volume, %	+6.32 (Pass)	+5 to +12
	Hardness, Pts	-1 (Pass)	-8 to +1
Nitrile (B)	Volume, %	+2.15 (Pass)	+1 to +6
	Hardness, Pts	-1 (Pass)	-3 to +6
Polyacrylic (C)	Volume, %	+4.14 (Pass)	+2 to +7
	Hardness, Pts	0 (Pass)	-4 to +4
Fluoroelastomer (H)	Volume, %	+4.02 (Pass)	+0.5 to +5
	Hardness, Pts	-2 (Pass)	-5 to +6
Silicone (J)	Volume, %	+27.43 (Pass)	+23 to +45
	Hardness, Pts	-18 (Pass)	-30 to -13
Ethylene-acrylic (R)	Volume, %	+14.95 (Pass)	+13 to +27
	Hardness, Pts	-11 (Pass)	-17 to -7

Table 4

Seal Material	Property	Results	Test Limits
Polyacrylic (A)	Volume, %	+6.74 (Pass)	+5 to +12
	Hardness, Pts	-3 (Pass)	-8 to +1
Nitrile (B)	Volume, %	+1.38 (Pass)	+1 to +6
	Hardness, Pts	0 (Pass)	-3 to +6
Polyacrylic (C)	Volume, %	+4.71 (Pass)	+2 to +7
	Hardness, Pts	-1 (Pass)	-4 to +4
Fluoroelastomer (H)	Volume, %	+3.68 (Pass)	+0.5 to +5
	Hardness, Pts	-3 (Pass)	-5 to +6
Silicone (J)	Volume, %	+24.2 (Pass)	+23 to +45
	Hardness, Pts	-16 (Pass)	-30 to -13
Ethylene-acrylic (R)	Volume, %	+14.4 (Pass)	+13 to +27
	Hardness, Pts	-9 (Pass)	-17 to -7

Table 5

Seal Material	Property	Results	Test Limits
ATRR-100 (Nitrile)	Volume, %	+2.94 (Pass)	+1 to +6
	Hardness, Pts	+3 (Pass)	-5 to +5
ATRR-200 (Polyacrylate)	Volume, %	+5.35 (Pass)	+3 to +8
	Hardness, Pts	+2 (Pass)	-5 to +5
ATRR-300 (Silicone)	Reversion	No Reversion	No Reversion
ATRR-400 (Fluoroelastomer)	Volume, %	+3.28	No Limits Report Only
	Hardness, Pts	0	
ATRR-500 (Ethylene-acrylic)	Volume, %	+11.15	No Limits Report Only
	Hardness, Pts	-4	

Table 6

Seal Material	Property	Results	Test Limits
ATRR-100 (Nitrile)	Volume, %	+2.36 (Pass)	+1 to +6
	Hardness, Pts	0 (Pass)	-5 to +5
ATRR-200 (Polyacrylate)	Volume, %	+5.60 (Pass)	+3 to +8
	Hardness, Pts	-2 (Pass)	-5 to +5
ATRR-300 (Silicone)	Reversion	No Reversion	No Reversion
ATRR-400 (Fluoroelastomer)	Volume, %	+2.86	No Limits Report Only
	Hardness, Pts	0	
ATRR-500 (Ethylene-acrylic)	Volume, %	+9.93	No Limits Report Only
	Hardness, Pts	-5	

Table 7 summarizes the excellent shear stability of a fluid of this invention when subjected to three different test procedures. The fluid subjected to these tests had a kinematic viscosity at 100°C of 7.49 and a Brookfield viscosity of 5640 at -40°C. The results shown in Table 7 are kinematic viscosities at 100°C. The Taper Roller Bearing Shear Test results met the Mercedes-Benz requirements of 6.0 cSt after 4 hours and 5.0 cSt after 20 hours of shearing.

Table 7

Test Procedure	Results	% Shear
FZG Shear Test, 20h, cSt	6.36	15.1
ASTM D-3945b (FISST), 20 cycles, cSt	6.68	10.8
Taper Roller Bearing Shear Test 4h, cSt	6.40	14.6
Taper Roller Bearing Shear Test 8h, cSt	6.03	19.5
Taper Roller Bearing Shear Test 20h, cSt	5.67	24.3

As used herein the term "oil-soluble" means that the substance under discussion should be sufficiently soluble at 20°C in the particular power transmission fluid composition being formulated pursuant to this invention base oil to reach at least the minimum concentration required to enable the substance to serve its intended function. Preferably the substance will have a substantially greater solubility in the fluid composition than this. However, the substance need not dissolve in the fluid composition in all proportions.

Each and every U.S. patent document referred to hereinabove is incorporated herein by reference as if fully set forth herein.

It will be readily apparent that this invention is susceptible to considerable modification in its practice. Accordingly, this invention is not intended to be limited by the specific exemplifications presented hereinabove. Rather, what is intended to be covered is within the spirit and scope of the appended claims.

#### Claims

1. A power transmission fluid composition which has, on a weight basis, an oil-soluble boron content of 0.001 to 0.1%, an oil-soluble phosphorus content of 0.005 to 0.2% and an oil-soluble metal content as metal-containing additive of no more than about 100 ppm and which comprises the following components:
  - a) at least about 70 wt% based on the total weight of the composition of an hydrogenated poly- $\alpha$ -olefin oligomer fluid having a kinematic viscosity of  $2 \times 10^{-6}$  to  $6 \times 10^{-6}$  m<sup>2</sup>/s (2 to 6 cSt) at 100°C;
  - b) on an active ingredient basis, 2 to 20 wt% based on the total weight of the composition of an acrylic viscosity index improver which is in the form of a solution with an inert solvent;
  - c) 4 to 25 wt% based on the total weight of the composition of an oil-soluble dialkyl ester of a C<sub>4</sub> to C<sub>14</sub>  $\alpha,\omega$ -dicarboxylic acid having a pour point of -45°C or lower;
  - d) a dispersant amount of an oil-soluble ashless dispersant;
  - e) a friction modifying amount an oil-soluble friction modifier; and
  - f) an oil-soluble inhibitor selected from foam inhibitors, copper corrosion inhibitors, rust inhibitors and oxidation inhibitors;

with the proviso that the power transmission fluid composition has (i) a kinematic viscosity of at least  $6.8 \times 10^{-6}$  m<sup>2</sup>/s (6.8 cSt) at 100°C, (ii) a Brookfield viscosity of 15 Pas (15,000 cP) or less at -40°C, (iii) a kinematic viscosity at 100°C of at least  $6.0 \times 10^{-6}$  m<sup>2</sup>/s (6.0 cSt) after 4 hours in the Volkswagen taper roller bearing shear stability test, and (iv) a kinematic viscosity at 100°C of at least  $5.0 \times 10^{-6}$  m<sup>2</sup>/s (5.0 cSt) after 20 hours in the Volkswagen taper roller bearing shear stability test.
2. The composition of claim 1 which is devoid of any sulfurized ester and of any sulfurized olefinic compound.
3. The composition of claim 1 or 2 wherein the ashless dispersant d) is a phosphorus-containing dispersant.
4. The composition of any one of claims 1 to 3 wherein the ashless dispersant d) is a phosphorus-containing dispersant and the composition further comprises a non-dispersant metal-free oil-soluble nitrogen- and phosphorus-containing antiwear/extreme pressure agent, the phosphorus content of the composition being provided by the phosphorus-containing dispersant and the antiwear/extreme pressure agent.
5. The composition of any one of claims 1 to 4 wherein the ashless dispersant d) is a boron- and phosphorus-containing dispersant.
6. The composition of claim 5 wherein the ashless dispersant d) is a boron- and phosphorus-containing succinimide dispersant.
7. The composition of claim 6 wherein the boron- and phosphorus-containing succinimide dispersant is formed by a process which comprises heating a succinimide ashless dispersant concurrently or in any sequence with one or more inorganic phosphorus compounds and with one or more boron compounds to a temperature at which an essentially solids-free composition is formed.
8. The composition of claim 7 wherein the boron- and phosphorus-containing succinimide dispersant is formed by a process which comprises heating an alkenyl succinimide dispersant in which the alkenyl group is derived from a polyolefin having a GPC number average molecular weight of 700 to 2100.



9. The composition of claim 8 wherein the boron- and phosphorus-containing succinimide dispersant is formed by a process which comprises heating a polyisobutenyl succinimide dispersant in which the alkenyl group is derived from polyisobutene having a GPC number average molecular weight of 800 to 1350.
10. The composition of claim 9 wherein the boron- and phosphorus-containing succinimide dispersant is formed by a process which comprises heating a polyisobutenyl succinimide dispersant in which the alkenyl group is derived from polyisobutene having a GPC number average molecular weight of 900 to 1100 concurrently or in any sequence with phosphorous acid,  $H_3PO_3$ , and with boric acid in the presence of water to a temperature at which an essentially solids-free composition is formed and then stripping off water from the essentially solids-free composition.
11. The composition of any one of claims 1 to 10 wherein component f) comprises (i) 0.1 to 1.0 wt% of a 1,3,5-thiadiazole copper corrosion inhibitor and (ii) 0.01 to 0.1 wt% of a calcium sulfurized alkylphenate, (i) and (ii) being the only sulfur-containing additive components in the composition.
12. The composition of any one of claims 1 to 11 wherein component c) is a dialkyl ester of adipic acid.
13. The composition of claim 12 wherein the dialkyl ester consists essentially of diisooctyl adipate.
14. The composition of any one of claims 1 to 13 wherein the hydrogenated poly- $\alpha$ -olefin oligomer fluid a) consists essentially of a mixture of a poly- $\alpha$ -olefin lubricating fluid with a viscosity of about  $4 \times 10^{-6} \text{ m}^2/\text{s}$  (4 cSt) at  $100^\circ\text{C}$  and a poly- $\alpha$ -olefin lubricating fluid with a viscosity of about  $6 \times 10^{-6} \text{ m}^2/\text{s}$  (6 cSt) at  $100^\circ\text{C}$ .
15. The composition of any one of claims 1 to 14 wherein the ashless dispersant d) is a boron- and phosphorus-containing dispersant which provides all of the boron content of the composition and wherein component f) comprises (i) 0.1 to 1.0 wt% of a thiadiazole copper corrosion inhibitor and (ii) 0.01 to 0.1 wt% of a calcium sulfurized alkylphenate, (i) and (ii) being the only sulfur-containing additive components in the composition.
16. The composition of any one of claims 1 to 15 wherein the ashless dispersant is a boron- and phosphorus-containing dispersant and wherein component f) comprises a foam inhibitor, a copper corrosion inhibitor, a rust inhibitor and an oxidation inhibitor.
17. The composition of any one of claims 1 to 16 which is devoid of any poly- $\alpha$ -olefin lubricating fluid comprising more than a minor amount by weight of species above hexamer, wherein the ashless dispersant d) is a boron- and phosphorus-containing dispersant, and wherein component f) comprises (i) a 2-mercapto-5-alkyldithio-1,3,5-thiadiazole or 2,5-bis(alkyldithio)-1,3,5-thiadiazole, (ii) a ring-alkylated diphenylamine, (iii) a sterically-hindered tertiary butyl phenol, (iv) a calcium sulfurized alkylphenate, (v) an alkyloxypropylamine, (vi) an aliphatic monocarboxylic acid, (vii) an alkyl glycol nonionic surfactant and (viii) a silicone foam inhibitor.
18. The composition of any one of claims 1 to 17 wherein the friction modifier e) comprises an N-aliphatic hydrocarbyl-substituted diethanol amine in which the N-aliphatic hydrocarbyl-substituent is a straight chain aliphatic hydrocarbyl group free of acetylenic unsaturation and having 14 to 20 carbon atoms.
19. An automatic transmission fluid composition which has, on a weight basis, an oil-soluble boron content of 0.001 to 0.1%, an oil-soluble phosphorus content of 0.005 to 0.2%, and an oil-soluble metal content as metal-containing additive of no more than about 100 ppm and which comprises the following components:
- at least about 70 wt% based on the total weight of the composition of a hydrogenated poly- $\alpha$ -olefin oligomer fluid, which: (1) has a viscosity of  $4 \times 10^{-6}$  to  $6 \times 10^{-6} \text{ m}^2/\text{s}$  (4 to 6 cSt) at  $100^\circ\text{C}$ ; (2) contains on a weight basis not more than a minor amount of species above hexamer, if any; and (3) is the only poly- $\alpha$ -olefin oligomer fluid in the composition;
  - on an active ingredient basis, 2 to 20 wt% based on the total weight of the composition of an acrylic viscosity index improver which is in the form of a solution with an inert solvent and which exhibits a permanent shear stability index of no higher than about 35 according to ASTM test method D-3945a;
  - 4 to 25 wt% based on the total weight of the composition of an oil-soluble dialkyl ester of a  $C_6$  to  $C_{10}$   $\alpha,\omega$ -dicarboxylic acid having a pour point of  $-45^\circ\text{C}$  or lower;
  - a dispersant amount of an oil-soluble phosphorus-containing ashless dispersant;
  - a friction modifying amount of an oil-soluble friction modifier; and
  - an oil-soluble foam inhibitor, an oil-soluble copper corrosion inhibitor, an oil-soluble rust inhibitor and an oil-soluble oxidation inhibitor; with the proviso that the power transmission fluid composition:

(A) has (i) a kinematic viscosity of at least  $6.8 \times 10^{-6} \text{ m}^2/\text{s}$  (6.8 cSt) at  $100^\circ\text{C}$ , (ii) a Brookfield viscosity of 15 Pas (15,000 cP) or less at  $-40^\circ\text{C}$ , (iii) a kinematic viscosity at  $100^\circ\text{C}$  of at least  $6.0 \times 10^{-6} \text{ m}^2/\text{s}$  (6.0 cSt) after 4 hours in the Volkswagen taper roller bearing shear stability test, and (iv) a kinematic viscosity at  $100^\circ\text{C}$  of at least  $5.0 \times 10^{-6} \text{ m}^2/\text{s}$  (5.0 cSt) after 20 hours in the Volkswagen taper roller bearing shear stability test; and

(B) passes all of the seal tests set forth in the DEXRON® III specifications of General Motors Corporation and all of the seal tests set forth in the MERCON® specifications of Ford Motor Company.

20. The composition of claim 19 wherein the oil-soluble phosphorus-containing ashless dispersant is an oil-soluble boron- and phosphorus-containing ashless dispersant; the friction modifier comprises an N-aliphatic hydrocarbyl-substituted diethanol amine in which the N-aliphatic hydrocarbyl-substituent is a straight chain aliphatic hydrocarbyl group free of acetylenic unsaturation and having 14 to 20 carbon atoms; and wherein component f) comprises (i) 0.1 to 1.0 wt% of a 1,3,5-thiadiazole copper corrosion inhibitor and (ii) 0.01 to 0.1 wt% of calcium sulfurized alkylphenate, (i) and (ii) being the only sulfur-containing additive components in the composition.
21. A composition in accordance with claim 20 wherein the boron content of the composition is provided by the oil-soluble boron- and phosphorus-containing ashless dispersant.
22. A composition in accordance with claim 20 or 21 wherein the phosphorus content of the composition is provided by the oil-soluble boron- and phosphorus-containing ashless dispersant.
23. A composition in accordance with claim 20, 21 or 22 wherein the calcium sulfurized alkylphenate is the only metal-containing additive component in the composition.

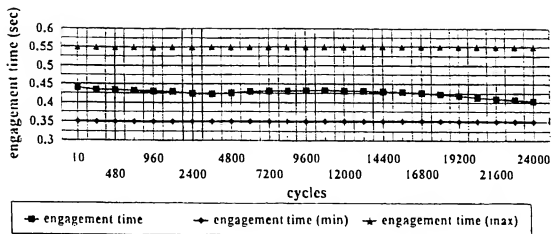


FIG. 1

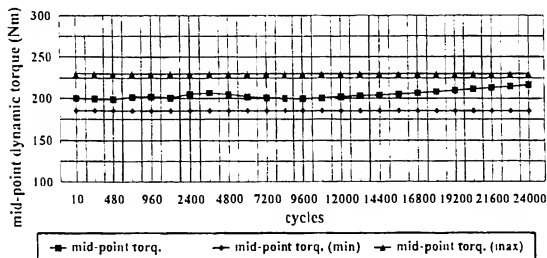


FIG. 2

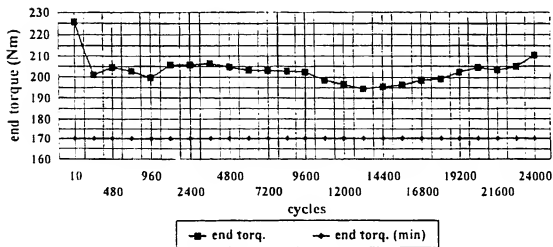


FIG. 3

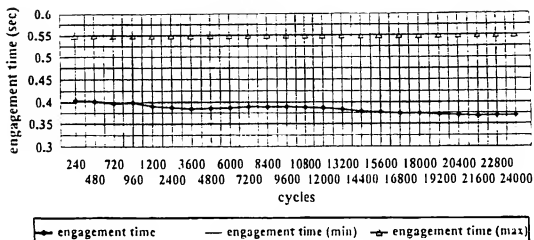


FIG. 4

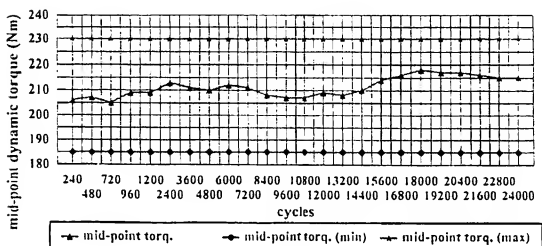
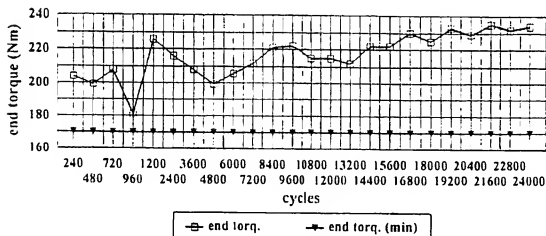


FIG. 5





## EUROPEAN PATENT APPLICATION

(88) Date of publication A3:  
11.06.1997 Bulletin 1997/24

(51) Int. Cl.<sup>5</sup>: C10M 169/04  
// C10N20:02, C10N40:04

(43) Date of publication A2:  
17.07.1996 Bulletin 1996/29

(21) Application number: 96300227.4

(22) Date of filing: 11.01.1996

(84) Designated Contracting States:  
BE DE ES FR GB IT

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(54) Synthetic power transmission fluids having enhanced performance capabilities

(57) A power transmission fluid composition which has, on a weight basis, an oil-soluble boron content of 0.001 to 0.1%, an oil-soluble phosphorus content of 0.005 to 0.2% and an oil-soluble metal content as metal-containing additive of no more than about 100 ppm and which comprises the following components:

a kinematic viscosity at 100°C of at least  $6.0 \times 10^{-6}$  m<sup>2</sup>/s (6.0 cSt) after 4 hours in the Volkswagen taper roller bearing shear stability test, and (iv) a kinematic viscosity at 100°C of at least  $5.0 \times 10^{-6}$  m<sup>2</sup>/s (5.0 cSt) after 20 hours in the Volkswagen taper roller bearing shear stability test.

a) at least about 70 wt% based on the total weight of the composition of an hydrogenated poly- $\alpha$ -olefin oligomer fluid having a kinematic viscosity of  $2 \times 10^{-6}$  to  $6 \times 10^{-6}$  m<sup>2</sup>/s (2 to 6 cSt) at 100°C;

b) on an active ingredient basis, 2 to 20 wt% based on the total weight of the composition of an acrylic viscosity index improver which is in the form of a solution with an inert solvent;

c) 4 to 25 wt% based on the total weight of the composition of an oil-soluble dialkyl ester of a C<sub>4</sub> to C<sub>14</sub>  $\alpha,\omega$ -dicarboxylic acid having a pour point of -45°C or lower;

d) a dispersant amount of an oil-soluble ashless dispersant;

e) a friction modifying amount an oil-soluble friction modifier; and

f) an oil-soluble inhibitor selected from foam inhibitors, copper corrosion inhibitors, rust inhibitors and oxidation inhibitors;

with the proviso that the power transmission fluid composition has (i) a kinematic viscosity of at least  $6.8 \times 10^{-6}$  m<sup>2</sup>/s (6.8 cSt) at 100°C, (ii) a Brookfield viscosity of 15 Pas (15,000 cP) or less at -40°C, (iii)



European Patent  
Office

## EUROPEAN SEARCH REPORT

Application Number  
EP 96 30 0227

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
D, X	US 5 089 156 A (D.R. CHRISOPE) * column 1, line 32 - column 2, line 3 * * column 2, line 54 - line 68 * * column 6, line 6 - line 41 * * column 7, line 11 - column 12, line 24; example 2 *	1-23	C10M169/04 //C10N20:02, C10H40:04
X	EP 0 453 114 A (TONEH CORP.) * page 2, line 30 - line 66 * * page 3, line 26 - page 4, line 17 * * page 4, line 44 - page 6, line 3; example 6; table 2 *	1-23	
A	US 4 519 932 A (N.E. SCHNUR) * column 4, line 44 - line 66 *	1, 19	
A	GB 2 267 098 A (ETHYL CORP.) * page 10, line 6 - line 15 *	1, 19	
A	GB 2 094 339 A (THE LUBRIZOL CORP.) * the whole document *	1-23	TECHNICAL FIELDS SEARCHED (Int.Cl.6)
A	WO 94 22990 A (ETHYL CORP.) * claim 1 *	1-23	C10H
The present search report has been drawn up for all claims			
Place of search		Date of completion of the search	Examiner
THE HAGUE		16 April 1997	Rotsaert, L
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X: particularly relevant if taken alone Y: particularly relevant if combined with another document of the same category A: technological background O: non-written disclosure P: intermediate document</p> <p>T: theory or principle underlying the invention E: earlier patent document, but published on, or after the filing date D: document cited in the application L: document cited for other reasons</p> <p>*: number of the same patent family, corresponding document</p>			

(19) United States

(12) Patent Application Publication

(10) Pub. No.: US 2003/0036488 A1

Yuki et al.

(43) Pub. Date: Feb. 20, 2003

(54) VISCOSITY INDEX IMPROVER AND LUBE OIL CONTAINING THE SAME

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(21) Appl. No.: 10/114,283

(22) Filed: Apr. 3, 2002

(30) Foreign Application Priority Data

Apr. 6, 2001 (JP) ..... JP2001-109164

Publication Classification

(51) Int. Cl.<sup>7</sup> ..... C10M 145/14(52) U.S. CL. .... 508/469; 508/470; 508/471;  
508/472

(57) ABSTRACT

A viscosity index improver, which comprises a polymer (A) having a solubility parameter of 8.6-9.4, a crystallizing initiation temperature of equal to or less than  $-15^{\circ}\text{C}$ ., and a steric hindrance factor (I<sup>2</sup>) of 0-13, said factor F being defined by the following equation:

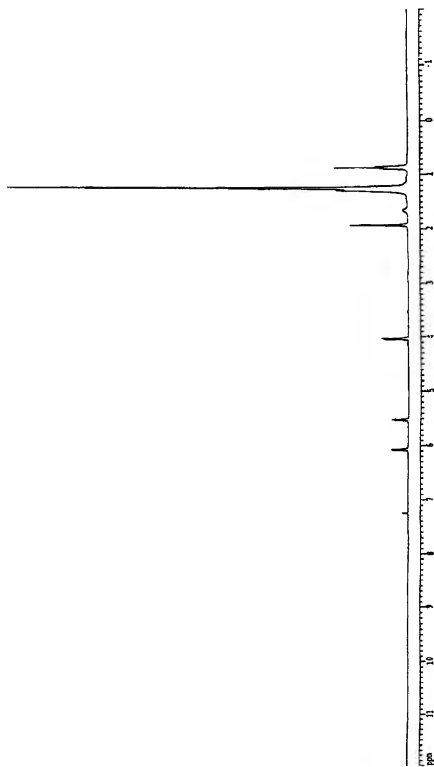
$F=4X+Y$  (1) wherein X and Y represent the total numbers of atoms at the 6th position and the 7th position, respectively, in the side chains; said polymer (A) having a Mw of 5,000-2,000,000 and comprising units of at least one monomer selected from the group consisting of:

(a) a monomer represented by the general formula:

$\text{Cl}_1-\text{C}(\text{R}^0)-\text{COO}-(\text{AO})_n-\text{R}$  (2) wherein R<sup>0</sup> is hydrogen atom or methyl group, R is a C<sub>1-20</sub>alkyl group, n is 0 or an integer of 1-20 giving 0-10 on average, A is an alkylene group containing 2-4 carbon atoms, plural A's in case of n being at least 2 are the same or different, and the polyoxyalkylene moiety (AO)<sub>n</sub> in case of the plural A's being different comprises random-wise or block-wise distributed oxyalkylene groups; (b) an alkyl alkenyl ether; (c) an alkenyl carboxylate; and (d) a nitrogen-containing unsaturated monomer.

The suitable monomers, 2-decyl-tetradecyl methacrylate and 2-decyl-tetradecyl acrylate compose the polymer (A), are also described.

**Fig. 1**  
 **$^1\text{H}$ -NMR**





**Fig. 2**  
 **$^{13}\text{C}$ -NMR**

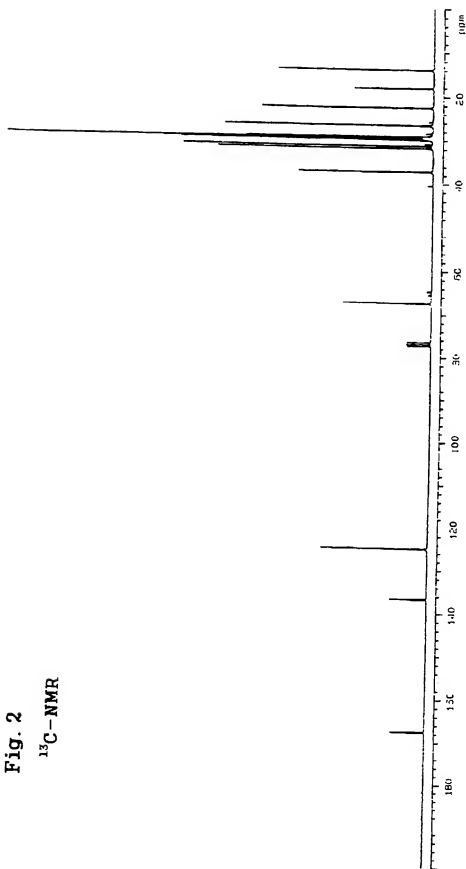
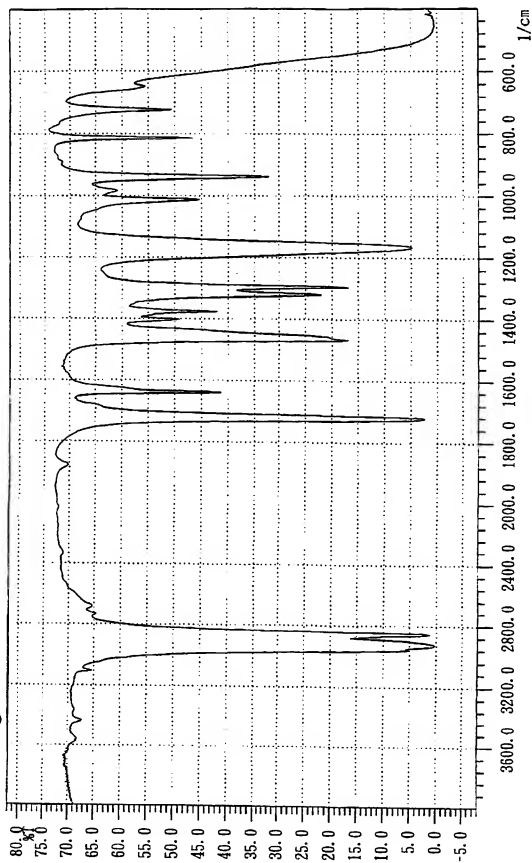


Fig. 3



# VISCOSITY INDEX IMPROVER AND LUBE OIL CONTAINING THE SAME

## BACKGROUND OF THE INVENTION

### [0001] 1. Field of the Invention

[0002] This invention relates to a viscosity index improver (hereinafter referred to as VII). More particularly, it relates to a VII for lube oils, such as engine oils, automatic transmission fluids (ATF), continuously variable transmission fluids (CVT), gear oils and hydraulic fluids.

### [0003] 2. Description of the Prior Art

[0004] As VIs to improve viscosity index (hereinafter referred to as VI) of lube oils, there have been known heretofore copolymers of  $C_{1-18}$  alkyl (meth) acrylates (I or instance, U.S. Pat. No. 5,622,924). The word, "(meth)acrylate" represents acrylate and/or methacrylate and also " $C_{1-18}$  alkyl" represents alkyl group containing 1-18 carbon atoms; and similar expressions are used hereinafter.

## SUMMARY OF THE INVENTION

[0005] It is an object of the present invention to provide a VII capable of imparting an improved VI to lube oil.

[0006] It is another object of this invention to provide a viscosity improver concentrate capable of imparting an improved VI to a lube oil.

[0007] It is still another object of the invention to provide a lube oil composition having an improved VI.

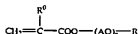
[0008] It is yet another object of the present invention to provide a monomer consisting of 2-decyl-tetradecyl methacrylate or 2-decyl-tetradecyl acrylate.

[0009] Briefly, these and other objects of this invention as hereinafter will become more readily apparent have been attained broadly by a VII, comprising a polymer (A) or (A11) as follows. Polymer (A) has a solubility parameter (hereinafter referred to as SP) of 8.6-9.4, a crystallizing initiation temperature (hereinafter referred to as Tc) of equal to or less than  $-15^{\circ}\text{C}$  and a steric hindrance factor F, defined by the following equation (1), of 0-13.

$$F = \frac{X}{Y} \quad (1)$$

[0010] In the equation (1), X and Y represent the total numbers of atoms at the 6th position and the 7th position, respectively, in the side chains, counted from the backbone.

[0011] Polymer (A) comprises units of at least one monomer selected from the group consisting of an acrylic monomer (hereinafter referred to as (a)) represented by the following general formula (2), an alkyl alkenyl ether (hereinafter referred to as (b)), an alkenyl carboxylate (hereinafter referred to as (c)) and a nitrogen-containing unsaturated monomer (hereinafter referred to as (d)).



[0012] In the general formula (2),  $\text{R}^0$  is hydrogen atom or methyl group, R is a  $C_{1-18}$  alkyl group, n is 0 or an integer of 1-20 giving 0-10 on average, and A is an  $C_{2-18}$  alkylene group.

[0013] Polymer (A) is preferably a copolymer (A11), comprising units of at least one monomer (a1) represented by the general formula (2) wherein R is a branched  $C_{1-18}$  alkyl group (hereinafter referred to as  $\text{R}^1$ ).

[0014] Copolymer (A11), in another aspect of this invention, comprises units of at least one monomer (a11) represented by the general formula (2) wherein R is a branched  $C_{2-18}$  alkyl group (hereinafter referred to as  $\text{R}^{11}$ ), and units of at least one other alkyl (meth)acrylate. Said (meth)acrylate (a11) is capable of providing a homopolymer having a Tc of equal to or less than  $5^{\circ}\text{C}$ .

[0015] Polymers (A) and (A11) have a weight-average molecular weight (hereinafter referred to as Mw) of usually 5,000-2,000,000.

[0016] In the above, "polymer" represents copolymer and/or homopolymer; and such expression is used hereinafter.

## BRIEF DESCRIPTION OF THE DRAWINGS

[0017] FIG. 1, FIG. 2 and FIG. 3 show the  $^1\text{H}$ -NMR spectrum, the  $^{13}\text{C}$ -NMR spectrum, and the IR spectrum of 2-decyl-tetradecyl methacrylate, respectively.

## DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS MONOMERS COMPOSING THE POLYMER (A)

[0018] The following monomers (a) to (m) compose the polymer (A).

[0019] (a) Acrylic monomers (hereinafter referred to as (a))

[0020] Monomers (a) are represented by the above-mentioned general formula (2). In the general formula (2), n is 0 or an integer of 1-20 (preferably 0-10) giving 0-10 (preferably 0-5) on average, particularly n is 0. Suitable  $C_{2-18}$  alkylene groups that is shown "A" in the formula (2), include ethylene, propylene, and 1,2-, 2,3-, 1,3- and 1,4-butylene groups, as well as combinations of two or more of these alkylene groups. Among alkylene groups, preferred are ethylene, propylene, 1,2-butylene and combinations of them.

[0021] In case of n is at least 2, the said A is represented as A'. Plural A's may be the same or different, and the polyoxy-alkylene moiety (A'O), in case of the plural A's being different can comprise random-wise and/or block-wise distributed oxyalkylene groups.

[0022]  $\text{R}^0$  is hydrogen atom or methyl group, preferably methyl group.

[0023] Suitable  $C_{1-18}$  alkyl groups (R) include, for example,

[0024] (1)  $\text{R}^1$ , namely branched  $C_{1-18}$  alkyl groups;

[0025] (2)  $C_{1-18}$  alkyl groups, such as methyl, ethyl, n- and i-propyl, and n-, i-, sec- and t-butyl groups;

[0026] (3) straight-chain and branched-chain  $C_{1-18}$  alkyl groups, such as n- and i-octyl, 2-ethylhexyl, n- and i-nonyl, n- and i-decyl, n- and i-dodecyl, 2-methylundecyl, n- and i-tridecyl, 2-methyl-dodecyl, n- and i-tetradecyl, 2-methyltridecyl, n- and i-pentadecyl and 2-methyltetradecyl groups;

- [0027] (4) straight-chain  $C_{10-19}$  alkyl groups, such as n-hexadecyl, n-octadecyl and n-nonadecyl groups;
- [0028] (5) straight-chain  $C_{20-40}$  alkyl groups, such as n-cicosyl, n-docosyl, n-tetracosyl and n-octacosyl groups; and
- [0029] (6) straight-chain and branched  $C_{5-9}$  alkyl groups, such as n-, i-, sec- and neo-pentyl, n- and i-hexyl 2-methylpentyl and n- and i-heptyl groups.
- [0030] Suitable branched  $C_{10-40}$  alkyl groups ( $R^1$ ) have usually 1-12 branchings, preferably 1 branching. Branched  $C_{10-40}$  alkyl groups ( $R^1$ ) are inclusive of branched  $C_{20-40}$  alkyl groups ( $R^{11}$ ) and branched  $C_{10-19}$  alkyl groups ( $R^{12}$ ).
- [0031] Illustrative of suitable groups  $R^{11}$  are, for example,

[0032] 1-alkyl groups (e.g., 1-ethyltetradecyl, 1-hexyltetradecyl, 1-octyldecyl, 1-butylcicosyl, 1-hexyltetradecyl, 1-octylhexadecyl, 1-decyltetradecyl, 1-undecyltridecyl groups, etc.);

[0033] 2-alkyl groups (e.g., 2-hexyltetradecyl, 2-ethyltetradecyl, 2-decyltetradecyl, 2-undecyltridecyl, 2-octylhexadecyl, 2-hexyloctadecyl, 2-dodecylhexadecyl, 2-tridecylpentadecyl, 2-decyltetradecyl, 2-tetradecyloctadecyl, 2-hexadecyloctadecyl, 2-tetradecylcicosyl and 2-hexadecylcicosyl groups, etc.);

[0034] 3-alkyl to 34-alkyl groups (e.g., 3-alkyl, 4-alkyl, 5-alkyl, 32-alkyl, 33-alkyl, 34-alkyl, etc.); and

[0035] alkyl groups containing one or more branchings (e.g., alkyl groups of oxalcohols corresponding to propylene oligomers (from heptamer to undecamer), ethylene/propylene (molar ratio 16/1-1/11) oligomers, iso-butylene oligomers (from pentamer to octamer),  $\alpha$ -olefine( $C_{5-20}$ )oligomers from tetramer to octamer, etc.).

[0036] Examples of suitable groups  $R^{12}$  include 2-alkyl groups (e.g., 2-hexyldecyl, 2-hexylundecyl, 2-octyldecyl, 2-octyldecyl, 2-butyldecyl, 2-butyltetradecyl, 2-methyltetradecyl, 2-methylhexadecyl groups, etc.).

[0037] Among these groups  $R^{11}$  and  $R^{12}$ , preferred in regard of VI and low viscosity even at low temperature are groups  $R^{11}$ , particularly those of  $C_{20-36}$ . More preferred are those of  $C_{22-29}$ , especially of  $C_{24}$ . Preferable types in this regard are 2-alkyl groups, represented by the general formula:



[0038] Wherein  $R^1$  and  $R^2$  are the same or different straight-chain  $C_{1-19}$  alkyl groups. The most preferred  $R^1$  is a dodecyl group. The most preferred  $R^2$  is a dodecyl group.

[0039] The most preferred  $R$  in the formula (2) is a 2-decyltetradecyl group.

[0040] Suitable acyclic monomers (a) include, for example, monomers of the general formula (2) wherein  $R$  is

a branched  $C_{10-40}$  alkyl group  $R^1$  (hereinafter referred to as (a1)),  $C_{1-9}$  alkyl (meth)acrylates (hereinafter referred to as (a2)),  $C_{6-19}$  alkyl (meth)acrylates (hereinafter referred to as (a3)), straight-chain  $C_{6-19}$  alkyl (meth)acrylates (hereinafter referred to as (a4)), straight-chain  $C_{20-40}$  alkyl (meth)acrylates (hereinafter referred to as (a5)) and  $C_{5-9}$  alkyl (meth)acrylates (hereinafter referred to as (a6)).

[0041] Monomers (a1) include monomers (a11) of the general formula (2) wherein  $R$  is a branched  $C_{20-40}$  alkyl group  $R^{11}$  and monomers (a12) of the general formula (2) wherein  $R$  is a branched  $C_{10-19}$  alkyl group  $R^{12}$ . Among these, preferred are monomers (a1), particularly monomers (a11).

[0042] Monomers (a11), having  $R^{11}$ , are capable of providing a homopolymer having a Tc of equal to or less than  $5^\circ\text{C}$ ., preferably equal to or less than  $0^\circ\text{C}$ ., more preferably equal to or less than  $-15^\circ\text{C}$ . Tc is measured with respect to a homopolymer prepared by polymerizing a particular monomer under the following conditions.

[0043] Into a reaction vessel equipped with a stirrer, a heating and cooling device, a thermometer, a dropping funnel and nitrogen gas inlet tube, 25 parts of toluene is charged. After the atmosphere in the vessel is replaced with nitrogen gas, a monomer solution comprising 100 parts of monomer, 0.3 parts of a dodecyl mercaptan (hereinafter referred to as DM) that is a chain transfer agent and 0.5 parts of a 2,2'-azo-bis-(2,4-dimethylvaleronitrile) (hereinafter referred to as ADVN) is added dropwise from the dropping funnel. This addition is made over a period of 4 hours. at  $85^\circ\text{C}$ ., in the absence of air. The reaction mixture is held at  $85^\circ\text{C}$ . for a period of 2 hours. so that the polymerization proceeds well. Thereafter, toluene is evaporated under reduced pressure, at  $130^\circ\text{C}$ ., for 3 hours, and a resultant homopolymer is obtained.

[0044] Illustrative of suitable monomers (a11) are 2-decyltetradecyl methacrylate (Tc= $-30^\circ\text{C}$ .), 2-tetradecyloctadecyl methacrylate (Tc= $3^\circ\text{C}$ .), 2-octyldecylhexyl (meth)acrylate, diethylene glycol mono-2-decyltetradecylether (meth)acrylate, dipropylene glycol mono-2-decyltetradecylether (meth)acrylate and dibutylene glycol mono-2-decyltetradecylether (meth)acrylate. Tc in the parentheses is Tc of the homopolymer comprises the monomer.

[0045] There may be used two or more of these monomers, for instance, combinations of (a1) and (a2) with or without (a3)/(a4), and combinations of (a1) and (a2) with or without at least one of (a3), (a12), (a4) and (a5).

[0046] (b) Alkyl alkenyl ethers (hereinafter referred to as (b))

[0047] Suitable monomers (b) include, for example one represented by the general formula  $R\text{---}O\text{---}D$ , wherein  $D$  is a  $C_{2-10}$  (preferably  $C_{2-4}$ , particularly  $C_{2-3}$ ) alkenyl group and  $R$  is a  $C_{1-40}$  (preferably  $C_{1-30}$ , particularly  $C_{1-20}$ ) alkyl group. Examples of the suitable alkenyl group include vinyl, (meth)allyl and (iso)propenyl groups. Examples of the alkyl group  $R$  in the general formula include the same alkyl group "R" in the general formula (2) mentioned above in the said monomer (a).

[0048] Examples of suitable ethers (b) are alkyl vinyl ethers, and alkyl (meth)allyl ethers. Preferred are methyl vinyl ether, ethyl vinyl ether, methyl allyl ether and ethyl allyl ether.

- [0049] (c) Alkenyl carboxylate (hereinafter referred to as (c))
- [0050] Suitable monomers (c) include, for example, ones represented by the general formula  $R-COO-D$ , wherein R and D are the same as "R" and "D" in the above-mentioned general formula of the monomer (b). Illustrative of suitable carboxylates (c) are vinyl acetate, vinyl propionate, vinyl hexanoate, vinyl 2-ethylhexanoate and vinyl n-octanoate. Preferred are vinyl acetate and vinyl propionate.
- [0051] (d) Nitrogen-containing unsaturated monomers (hereinafter referred to as (d))
- [0052] Suitable monomers (d) are inclusive of amino-containing monomers (d1), amide-containing monomers (d2), and nitro-containing monomers (d3).
- [0053] Suitable monomers (d1) include primary, secondary and tertiary amino-containing aliphatic monomers, for example,
- [0054] mono- $C_{3-6}$  alkenyl amines (e.g., (di) (meth) allyl amines, crotyl amine, etc.), amino-containing acrylic monomers, for instance, amino- $C_{3-6}$  alkyl-(meth)acrylates (e.g., aminoethyl and aminopropyl (meth)acrylate, etc.) mono- and di- $C_{3-6}$  alkyl-amino  $C_{3-6}$  alkyl (meth)acrylates (e.g., (di)methyl-aminoethyl, (diethylaminoethyl, (di)butylaminoethyl and (di)methylaminopropyl (meth)acrylate, etc.);
- [0055] primary, secondary and tertiary amino-containing aromatic monomers, for example, aminostyrenes (e.g., (dimethylamino)styrene, phenylaminostyrene, etc.), (meth)acrylamides (e.g., 4- and 2-phenylaminophenyl (meth)acrylamide, etc.);
- [0056] amino-containing heterocyclic monomers, for example, morpholino  $C_{3-6}$  alkyl (meth)acrylates, (e.g., morpholinoethyl (meth) acrylate, etc.), vinylpyridines, (e.g., 4- and 2-vinylpyridine, N-vinylpyrrole and N-vinyl(thio)pyrrolidone, etc.).
- [0057] Suitable amide-containing monomers (d2) include
- [0058] (meth)acrylamide; and
- [0059] N-vinyl-carbamamides (e.g., N-vinyl-formamide, N-vinyl-acetoamide, N-vinyl-n- and i-propionamide, N-vinylhydroxyacetamide, etc.).
- [0060] Examples of nitro-containing monomers (d3) are nitrostyrenes, (e.g., 4-nitrostyrene, etc.).
- [0061] Among monomers (d), preferred are monomers (d1). More preferred are tertiary amino-containing acrylic monomers, particularly dimethylaminoethyl, diethylaminoethyl and morpholinoethyl (meth)acrylates.
- [0062] (e) Aliphatic hydrocarbon vinyl monomers (hereinafter referred to as (e))
- [0063] Suitable monomers (e) include, for example,  $C_{3-20}$  alkenes (e.g., ethylene, propylene, butene, isobutylene, pentene, heptene, diisobutylene, octene, dodecene, octadecene, etc.) and  $C_{4-12}$  alkadienes (e.g., butadiene, isoprene, 1,4-pentadiene, 1,6-heptadiene, 1,7-octadiene, etc.).
- [0064] (f) Alicyclic hydrocarbon vinyl monomers (hereinafter referred to as (f))
- [0065] Suitable monomers (f) include, for example, cyclohexene, (di)cyclopentadiene, pinene, limonene, indene, vinylcyclohexene, ethylidenecyclohexene.
- [0066] (g) Aromatic hydrocarbon vinyl monomers (hereinafter referred to as (g))
- [0067] Suitable monomers (g) include, for example, styrene,  $\alpha$ -methylstyrene, vinyltoluene, 2,4-dimethylstyrene, 4-ethylstyrene, 4-isopropylstyrene, 4-butylstyrene, 4-phenylstyrene, 4-cyclohexylstyrene, 4-benzylstyrene, 4-crotylbenzene and 2-vinylnaphthalene.
- [0068] (h) Vinyl ketones (hereinafter referred to as (h))
- [0069] Suitable monomers (h) include, for example,  $C_{3-10}$  alkyl or  $C_{6-10}$  aryl vinylketones (e.g., methylvinylketone, ethylvinylketone, phenylvinylketone, etc.).
- [0070] (i) Vinyl monomers having epoxy group (hereinafter referred to as (i))
- [0071] Suitable monomers (i) include, for example, glycidyl(meth)acrylate and glycidyl(meth)allyl ether.
- [0072] (j) Vinyl monomers having halogen (hereinafter referred to as (j))
- [0073] Suitable monomers (j) include, for example, vinyl chloride, vinyl bromide, vinylidene chloride, (meth)allyl chloride, styrene halide (e.g., dichlorostyrene, etc.).
- [0074] (k) Esters consisting of unsaturated polycarboxylic acid (hereinafter referred to as (k))
- [0075] Suitable monomers (k) include, for example, alkyl, cycloalkyl or aralkyl esters of unsaturated polycarboxylic acid. Among these esters, preferred are,  $C_{2-20}$  alkyl diester consisting of unsaturated dicarboxylic acid such as maleic acid, fumaric acid, itaconic acid, (e.g., dimethylmaleate, dimethylfumarate, diethylmaleate, dioctylmaleate, etc.). (l) vinyl monomers having hydroxyl group (hereinafter referred to as (l))
- [0076] Suitable monomers (l) include, for example,
- [0077] aromatic vinyl monomer having hydroxyl group (e.g., p-hydroxystyrene, etc.), hydroxy- $C_{3-6}$  alkyl(meth)acrylate (e.g., 2-hydroxyethyl(meth)acrylate, 2- or 3-hydroxypropyl(meth)acrylate, etc.);
- [0078] mono- or di-hydroxy- $C_{3-4}$  alkyl substituted (meth)acrylamide (e.g., N,N'-dihydroxymethyl(meth)acrylamide, N,N'-dihydroxypropyl (meth)acrylamide, N,N'-di-2-hydroxybutyl(meth)acrylamide, etc.);
- [0079] vinyl alcohol, that is obtained by hydrolysis of vinyl acetate;
- [0080]  $C_{3-12}$  alkenol (e.g., (meth)allyl alcohol, crotyl alcohol, iso-crotyl alcohol, 1-octenol, 1-undecanol, etc.);
- [0081]  $C_{4-12}$  alkenediol (e.g., 1-butene-3-ol, 2-butene-1-ol, 2-butene-1,4-diol, etc.);
- [0082] hydroxy- $C_{3-6}$  alkyl- $C_{3-10}$  alkenyl ether (e.g., 2-hydroxyethyl-propenyl ether, etc.);
- [0083] polyvalent alcohol having 3-8 hydroxy groups;

[0084] alkane polyol;

[0085] its intra- or inter-molecular dehydration product; and

[0086] C<sub>3-10</sub> alkenyl ether and (meth) acrylate, of a saccharide, for example, glycerol, pentaerythritol, sorbitol, sorbitan, diglycerol, and sucrose (e.g., sucrose (meth)allyl ether, etc.).

[0087] (m) vinyl monomers having carboxylic acid group (hereinafter referred to as (m))

[0088] Suitable monomers (m) include,

[0089] vinyl monomers having monocarboxylic acid group, for instance, unsaturated monocarboxylic acid (e.g., (meth)acrylic acid,  $\alpha$ -methyl(meth)acrylic acid, crotonic acid, cinnamic acid, etc.);

[0090] mono C<sub>3-8</sub> alkyl ester of unsaturated dicarboxylic acid (e.g., mono-alkyl maleate, mono-alkyl fumarate, mono-alkyl itaconate, etc.); and

[0091] vinyl monomers having dicarboxylic acid group (e.g., maleic acid, fumaric acid, itaconic acid, citraconic acid, etc.).

[0092] When VII is required property of a detergent, it is preferred that the polymer (A) comprises units of (d). When VII is not required property of a detergent, the monomer of (d) is not necessary to comprise the polymer (A).

#### POLYMER (A)

[0093] Several kinds of monomers that compose (A) include, preferably, at least (a), at least (b) or at least (a) and (b). The sum amount of (a) and (b), preferably at least 30%, more preferably 50-100%, particularly 80-100% against total amount of monomer(s) to be used for synthesis (A) (% stands for weight percentages hereafter, unless it is specifically mentioned otherwise). With regard to the ratio of (a) and (b), (a)/(b) is generally 30-100/0-70, preferably 50-100/0-50. If (c) and/or (d) is used together with (a) and/or (b), the amount of (c) preferably at most 45%, particularly at most 40%, and the amount of (d), preferably at most 12%, particularly at most 10%, against total amount of several monomers to be used for synthesis (A).

[0094] If (d) to (m) is employed by requirement, together with the monomers (a) to (c) for synthesis (A), the sum amount, if plural kinds of monomers (d) to (m) are employed, or the amount if single monomer selected from the group consisting of (d) to (m) is employed, is preferably 0-20%, particularly 0.1-10% against total weight of monomers (a) to (m)) to be used for synthesis (A).

[0095] The polymer (A1) contains generally 5-90%, preferably 10-80%, particularly 10-60%, most particularly 10-45% of units of (a1), and contain generally 10-60%, preferably 20-50%, particularly 20-45% of units of (a2). (A1) contains generally 0-85%, preferably 10-70%, particularly 10-60% of units of (a3) and/or (a4) (in particular, such

monomers having 10-18 carbon atoms). (A1) contains preferably 0-20%, more preferably 0-10% of units of (a5) and/or (a6).

[0096] In addition to (A1), example of the polymer (A) contains 5-20% of units of (a2), 30-70% of units of (a3), and 5-20% of units of (a4). Other examples of the polymer (A) are homopolymers comprises the monomer (b), such as homopolymer of methyl vinyl ether, homopolymer of the monomer that has general formula (2) and R is branched-alkyl group having 4-8 carbon atoms, and homopolymer of ethylene glycol mono-2-ethylhexyl-methacrylate, and the like.

[0097] The polymer (A) has a weight average molecular weight (Mw) of generally 5,000 to 2,000,000, preferably 8,000 to 500,000, more preferably 10,000 to 250,000. If Mw is 5,000 or more, (A) has adequate capability of increasing viscosity so that usually oil dose not need excess amount of (A). If Mw is 2,000,000 or less, (A) has adequate shear stability. Mw is measured by gel permeation chromatography using calibration curve of polystyrene.

[0098] The polymer (A) has a SP value of generally 8.6-9.4, preferably 9.0-9.35, particularly 9.1-9.3. If SP is between the above range, (A) has an adequate solubility to base oil and also adequate ability of improving VI. The SP value in the present invention is one measured by the Fedors method [Polym. Eng. Sci. 14 (2) 132, (1974)].

[0099] (A) has a Tc of generally equal to or less than -15° C., preferably equal to or less than -17.5° C., particularly -20 to -70° C., more particularly -35 to -70° C. If Tc is equal to or less than -15° C., (A) does not crystallize at low temperature, so that (A) has an excellent low temperature behavior. Tc value is measured using differential scanning calorimeter "UNIX DSC" (PERKIN-ELMER Corp.) applying 5 mg of polymer as a specimen, measuring the crystallizing initiation temperature (Tc) under cooling from 100 ° C. to -45° C. at a rate of -10° C./min.

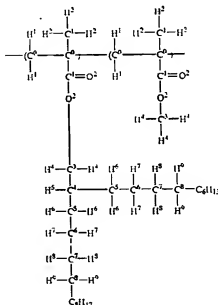
[0100] Further, (A) has a steric hindrance factor, F of generally 0-13, preferably 0-12.5, more preferably 0-10, particularly 0-8, more particularly 0-7. The F is defined the above-mentioned equation (1). Namely, considering a monomeric unit constituting polymer (A), X represents the total numbers of atoms at the sixth position in a side chain from the backbone. Y represents the total numbers of atoms at the seventh position atom in a side chain. If monomeric unit has plural side chains, X and Y are counted respective side chain and added to the total number. F<sup>0</sup> is the sum of four times X<sup>0</sup>, and Y<sup>0</sup>. The position is counted from the backbone (as shown in the following example) that a particular side chain bonded with, is assigned the number 0, and goes sequentially to the direction to outside of the particular side chain. The total number X and also Y are simply the sum of the atoms, that is, the kind of atom does not affect the total number. When the polymer (A) is copolymer, F is the average of F<sup>0</sup> of each monomer unit calculated based on the molar fractions of each monomer unit in the copolymer. The F briefly expresses degree of steric hindrance of side chain in the polymer. The greater F means the more degree of steric hindrance.

[0101] Following is an example of calculating F. A number of the right shoulder of atoms shows the position of atoms counted from backbone.

## Example Copolymer

2-Decyl-tetradecyl Methacrylate/Methyl Methacrylate=40/60 (molar ratio)

[0102]



[0103] The left-hand side-chain: 2-decyl-tetradecyl methacrylate residue. The total number of atoms at the sixth position = 6 (i.e., total number of atoms suffixed 6 at their right shoulder). The total number of atoms at the seventh position = 6

$$F^6=6 \times 4 + 6 = 30$$

[0104] The right-hand side-chain: methyl methacrylate residue. The total number of atoms at the sixth position = 0. The total number of atoms at the seventh position = 0

$$F^6=0 \times 4 + 0 = 0$$

[0105] Molar ratio = 40:60

$$F=30 \times 0.4 + 0 \times 0.6 = 12$$

[0106] If the F is 0-13, steric hindrance around backbone is small. Consequently, the polymer is easy to come to shrink at low temperature, and viscosity index becomes larger and viscosity at low temperature becomes low.

[0107] Means to adjust Mw and also the above-mentioned physical properties of polymer (A) in the present invention, is as follows. The Mw can be adjusted, for example, by changing temperature, monomer concentration (solvent concentration), quantity of catalyst and quantity of chain transfer agent, at polymerization. The SP value can be adjusted by selecting adequate kind of monomers and choosing their molar ratio by calculating SP value of the intended polymer using SP value of each constituting unit (such SP value is calculated by the Fedors method). For example, SP value of polymer can be adjusted by selecting monomer(s) having appropriate length of alkyl group(s). The longer such alkyl length is, the smaller SP of polymer becomes. Adversely, the

shorter such alkyl length is, the larger SP of polymer becomes. The Tc can be adjusted by selecting appropriate length of a methylene-chain existing in backbone and/or side-chain of polymer. For example, Tc becomes higher if the monomer having longer methylene-chain at an alkyl group in its side chain, is employed. Adversely, Tc becomes lower if the monomer having shorter methylene-chain at an alkyl group in its side chain, is employed. The F can be adjusted by selecting kinds of monomer and their molar ratio. For example, the F becomes smaller when employed more quantity of monomer(s) having less number of atoms at the sixth or the seventh position.

[0108] The polymer has HLB value of preferably 0.5-6, more preferably 1-5.5, particularly 1.5-5. If HLB is in this range, in particular, anti-emulsification is preferable. The above HLB value is calculated using HLB definition of Oda method based on a general concept of organic and inorganic nature of organic compound ("New Introduction to Surface Active Agents" T. FUJIMOTO, SANYO CHEMICAL INDUSTRIES, LTD. P 197-201).

## COPOLYMER (A11)

[0109] Another component of the present invention is the copolymer (A11). The copolymer (A11) contains generally 5-90%, preferably 10-80%, more preferably 10-70%, particularly 10-60%, more particularly 10-45% of units of (a11). The copolymer (A11) contains generally 5-95%, preferably 20-90%, more preferably 30-90%, particularly 40-90%, more particularly 55-90% of units of alkyl(meth)acrylates that are other than (a11). The expression "alkyl (meth)acrylates that are other than (a11)" means such acrylates are without the definition of the monomer group (a11); and similar expression is used hereinafter.

[0110] The monomers that are other than (a11), include the above-mentioned monomer (a2), (a3), (a12), (a4) and (a5). The copolymer (A11) includes generally 10-60%, preferably 20-50%, particularly 25-45% of units of (a2). The copolymer (A11) includes generally 0-85%, preferably 10-70%, particularly 10-60% of total units of (a3), (a12), (a4) and (a5).

[0111] In one most preferable embodiment, the copolymer (A11) is prepared by polymerizing 10-40% 2-decyl-tetradecyl methacrylate, 20-45% methyl methacrylate and 10-60% alkyl (meth) acrylates that are within the groups of (a3) and (a4) and also have C<sub>10-18</sub> straight-chain alkyl group.

[0112] If VII is required the property of a detergent as well as VI, in one preferable embodiment, the polymer (A11) also include the 0.1-10% (d) based on the total weight of monomers consisting (A11), especially, one or several monomer(s) selecting from the group consisting of dimethylaminoethyl (meth)acrylate, diethylaminoethyl (meth)acrylate and morpholinoethyl (meth)acrylate; the said three compounds are within the monomer (d).

[0113] The preferable Mw, SP, Tc and the F of the copolymer (A11), are the same range of ones of the polymer (A) as described above.

[0114] As the VII of the present invention, (A11) can be used by itself or (A11) can be used together with (A) that is other than (A11). A ratio of such combined usage is preferably (A11)/(A) other than (A11)=100/(0-20/80, more preferably 100(A)-70/30).

# PREPARATION OF THE POLYMERS (A) AND (A11)

[0115] The polymers (A) and (A11) of the present invention can be prepared by conventional methods well known to those of skill in the art. For instance, the polymer is prepared by radical polymerization of above-mentioned monomer(s) with solvent and polymerization catalyst.

[0116] The solvent includes, for example, aromatic compounds such as aromatic solvents having 7-15 carbon atoms (e.g., toluene, xylene, ethylbenzene, alkylbenzene having 9-10 carbon atoms, mixtures of trimethyl benzene, ethyl-toluene, etc.); ketone solvents (e.g., butanone, etc.); and mineral oils such as solvent refining oils, paraffin oils, isoparaffin containing and/or hydrogenolysis high viscosity index oils, hydrocarbon synthetic lubricants (e.g., poly  $\alpha$ -olefinic synthetic lubricant), ester synthetic lubricants, naphthene oils, and the like.

[0117] The polymerization catalyst includes, for example, azo catalyst (e.g., 2,2'-azo-bis-isobutyronitrile, 2,2'-bis-(2-methyl) butyronitrile, ADVN, dimethyl 2,2'-azo-bis-isobutyrate, etc.); and peroxide catalyst (e.g., t-butyl-peroxy-pivalate, t-hexyl-peroxy-pivalate, t-butyl-peroxyneodecanoate, t-butyl-peroxyneodecanoate, t-butyl-peroxy-2-ethylhexanoate, t-butyl-peroxyisobutyrate, t-amyl-peroxy-2-ethylhexanoate, 1,1,3,3-tetramethylbutyl-peroxy-2-ethylhexanoate, dibutyl-peroxytrimethyl adipate, benzoyl peroxide, cumyl peroxide, lauryl peroxide, etc.).

[0118] Further, if necessary, chain transfer agent (e.g., alkyl mercaptan having 2-20 carbon atoms, mercaptoacetic acid, mercapropionic acid, triethylene glycol dimercaptan, etc.) can be used in the synthesis.

[0119] The concentration of monomer(s) is preferably 40-95%, more preferably 60-90% based on weight of all chemicals including solvent in synthesis. The concentration of polymerization catalyst is preferably 0.1-5%, more preferably 0.15-0.5% based on weight of all monomer(s) in synthesis. The concentration of chain transfer agent is preferably 0-5%, more preferably 0-3% based on weight of all monomer(s) in synthesis.

[0120] The polymerization temperature is preferably 50-140° C., more preferably 70-120° C.

[0121] In addition, polymerization reaction can be bulk polymerization, emulsion polymerization or suspension polymerization in addition to the above-mentioned solution polymerization. Copolymerization can be by random copolymerization or alternating copolymerization, preferably random copolymerization. And also graft copolymerization or block copolymerization can be employed.

## THE VISCOSITY INDEX IMPROVER

[0122] The viscosity index improver (VII) of the present invention, can be a solvent-free polymer (A1) or (A11), or can be a solution of the polymer (A) or (A11). The solution of the polymer prepared by solution polymerization, can be used as VII concentrates. In other embodiment, a diluent can also be added to a substantially solvent-free polymer, usually by dissolving the substantially solvent-free polymer in an appropriate diluent, making VII concentrates. The solution of the polymer, namely VII concentrate is preferable.

Because, the polymer dissolves easily in base oil, if the polymer is diluted with diluent beforehand.

[0123] Examples of the diluents (hereinafter referred as (C)) are  $C_{6-18}$  aliphatic hydrocarbons (e.g., hexane, heptane, cyclohexane, octane, decalin, kerosene, etc.), the above-mentioned aromatic compound and mineral oils. A preferable diluent among these examples is mineral oil. The VII concentrates of the present invention, contains VII of preferably 10-90%, more preferably 30-80% and also contains diluent of preferably 10-90%, more preferably 20-70%.

## THE LUBE OIL COMPOSITION

[0124] Base oil in which VII of the present invention is added, is not particularly limited. Preferably, such base oil has a kinematic viscosity at 100° C. of, typically 1-15 mm<sup>2</sup>/s, more often 2-5 mm<sup>2</sup>/s. Preferably, such base oil has a VI value of typically at least 80, more often at least 100. The finished lube oil composition that is added the VII of the present invention into base oil, is improved to have larger VI and shows improved fuel efficiency.

[0125] In addition, such base oil has a cloud point (defined in JIS K2269) of, preferably equal to or less than -5° C., more preferably equal to or less than -10° C., particularly equal to or less than -15° C. If a cloud point of base oil is in the range mentioned above, quantities of deposition of wax is so small at low temperature, that viscosity behavior at low temperature is excellent. Such base oil includes, for example, mineral oils that is mentioned above. Preferable mineral oils are high viscosity index oils contained isoparaffin and/or manufactured by hydrocracking. Normally, the lube oil composition of present invention include 0.5-30% of the polymer (A) or (A11).

[0126] In one embodiment, the finished lube oil composition is intended as engine oil, preferably, 0.5-15% of the (A) or (A11), are added to base oil having a 3-10 mm<sup>2</sup>/s kinematic viscosity at 100° C. In another embodiment, the finished lube oil composition is intended as gear oil, preferably, 3-30% of the (A) or (A11), are added to base oil having 3-10 mm<sup>2</sup>/s a kinematic viscosity at 100° C. In yet another embodiment, the finished lube oil composition is intended as automatic-transmission fluid (e.g., ATF, CTFV etc.), preferably, 2-25% of the (A) or (A11), is added to base oil having 2-6 mm<sup>2</sup>/s a kinematic viscosity at 100° C. In further embodiment, the finished lube oil composition is intended as traction oil, preferably, 0.5-15% of the (A) or (A11), are added to base oil having 1-5 mm<sup>2</sup>/s a kinematic viscosity at 100° C. In yet further embodiment, the finished lube oil composition is intended as hydraulic oil, preferably, 0.5-25% of the (A) or (A11), is added to base oil having 1-10 mm<sup>2</sup>/s a kinematic viscosity at 100° C.

[0127] The lube oil compositions of this invention containing VII of (A) or (A11), may further contain, optionally, another kind of additives. The examples of such another kind of additives are copolymers of alkyl (meth)acrylate (other than such copolymer classified (A)); such copolymers are hereinafter referred to as (B). Examples of (B) are copolymers comprise units derived from (a), and such copolymers have at least one of SP, Te, F or Mw of without the aforesaid range that preferable (A) are encompassed. Preferable monomers compose (B), are the monomers within a group selecting from the group consisting of (a2), (a3), (a4), (a5), and (a6), that are included the above-



mentioned monomer group (a), and are the monomers from any group of (a2) to (a6). In one preferred embodiment, the copolymer (herein after referred to as (B1)) is composed of (a2) and (a3), or composed of (a2) and (a4), or composed of (a2), (a3) and (a4). In another preferred embodiment, the copolymer (hereinafter referred to as (B2)) is composed of two or more kind of monomers selecting from (a3) and/or (a4). In the (B1), the monomer ratio of (a2)/(a3)+(a4) is preferably (1-40)/(60-100), more preferably (5-35)/(65-95). In one particular embodiment of (B2), at least one kind of monomer composing (B2) has one having 12 to 18 carbon atoms, and average carbon atoms of all the monomers (B2) is 12 to 16, and the content of a branched-alkyl group is 0-30 mole %.

[0128] In one particular embodiment, the copolymer (B1) comprises (a2), (a3) and (a4), for example, copolymers of methyl methacrylate/dodecyl methacrylate/tetradecyl methacrylate/hexadecyl methacrylate (0-20%/20-45%/20-45%/0-20%). In one particular embodiment, the copolymer (B2) comprises (a3) and (a4), for example,

[0129] copolymers of dodecyl methacrylate/hexadecyl methacrylate (10-50%/50-90%), that have an average carbon atoms of 12.3-13.8, and have branched-alkyl group contents of 0 mol %;

[0130] copolymers comprises two kinds of monomers of (a3), for example, copolymers of dodecyl methacrylate/tetradecyl methacrylate (90-70%/10-30%), that have an average carbon atoms of 12.2-12.6, and that have branched-alkyl group contents of 0 mol %; and

[0131] copolymers of dodecyl acrylate/dodecyl methacrylate (10-40%/90-60%), that have an average carbon atoms of 12, and have branched-alkyl group contents of 0 mol %.

[0132] As the additional VII, (B) may use alone, or may use more than two kinds together. Mw of (B) is preferably 5,000-1,000,000, more preferably 10,000-250,000.

[0133] The lube oil composition of the present invention may contain further alkyl (meth)acrylate ester copolymers (B 11) other than the copolymer (A11).

[0134] In one embodiment, (B11) include alkyl (meth)acrylate ester copolymers that comprise (a11) of less than 5% or of greater than 90%. In another embodiment, (B11) include copolymers within the definition of (B) and comprise the units of the monomers (a11) of less than 5% or of greater than 90%. Preferable monomers compose (B11), are the same monomers as the ones that (B) are composed of, which are described above. Preferable (B11) has the same Mw range as the (B) has, which are also described above.

[0135] (B11) can be prepared by the same method as one for (A) preparation, mentioned above.

[0136] The (B) or (B11) can be mixed to (A) or (A11) in advance, then add to a base oil. And also, (B) or (B11), and (A) or (A11) can be separately added to a base oil.

[0137] The total amount of the (B) and (A), or (B) and (A11), to be added to a base oil is the same preferable range as the one of (A) or (A11), above-mentioned.

[0138] The lube oil composition of this invention may further contain one or more additives usually used in a lube

oil. Such additives include, for example, detergents, also referred to as an overbased or neutral metal salt (e.g., overbased alkali or alkaline earth metal salts of a sulfonate, phenate, naphthate, salicylate, carbonate, or mixtures thereof, etc.), dispersants (e.g., succinimide type; bis type, mono type and borate type, Mannich dispersants, etc.), antioxidants (e.g., hindered phenolic antioxidants, secondary aromatic amine antioxidants, etc.), friction modifier (e.g., long chain fatty acids; oleic acid, long chain fatty acid esters; oleate, long chain amines; oleylamine, long chain amide; oleylamide, etc.), antiwear agents (e.g., molybdenum dihydro phosphite, molybdenum dihydro carbamate, zinc dialkyl dithiophosphate, etc.), extreme-pressure agents (e.g., sulfur phosphide compounds, sulfur compounds, phosphide compounds, chloro compounds, etc.), antifoam agents (e.g., silicone oil, metallic soap, fatty acid ester, phosphate compounds, etc.), demulsifying agents (e.g., ictra ammonium salt compounds, sulfated oil, phosphate compounds, etc.) and corrosion inhibitors (e.g., nitrogen compound; benzotriazole, 1,3,4-thiadiazolyl-2,5-bis dialkyl dithiocarbamate, etc.).

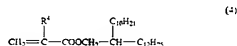
[0139] These additives can be used in such amounts: 0-20%, preferably 0.1-10% of the detergent; 0-20%, preferably 2.0-10% of the dispersant; 0-5%, preferably 0.1-3% of the antioxidants; 0-5%, preferably 0.1-1% of the friction modifier; 0-5%, preferably 0.1-3% of the antiwear agent; 0-20%, preferably 1.0-10% of the extreme-pressure agent; 2-1000 ppm, preferably 10-700 ppm of the antifoam agent; 0-3%, preferably 0-1% of the demulsifying agent; and 0-5%, preferably 0-2% of the corrosion inhibitor.

[0140] Lube oil compositions of this invention are useful as engine oils (such as an engine for means of transportation and engine for machine tools), gear oil, transmission lube oil (particularly, ATF and fluid for CVT), traction oil, shock-absorber oil, power steering oil, and the like.

## 2-DECYL-TETRADECYL (METH)ACRYLATE, AND ITS POLYMER

[0141] Another component of the present invention is a monomer of 2-decyl-tetradecyl (meth)acrylate (hereinafter referred as DTD), a homopolymer of the DTD and the copolymers comprising of the units of DTD.

[0142] The 2-decyl-tetradecyl (meth)acrylate is presented by the general formula (4):



[0143] In the formula (4), R<sup>1</sup> is methyl group (i.e., 2-decyl-tetradecyl methacrylate) or R<sup>1</sup> is hydrogen atom (i.e., 2-decyl-tetradecyl acrylate).

[0144] A DTD can be prepared by an esterification using 2-decyl-tetradecyl alcohol and (meth) acrylic acid, or can be prepared by a transesterification using 2-decyl-tetradecyl alcohol and (meth)acrylic acid derivatives. The 2-decyl-tetradecyl alcohol is commercially available, for example, under the trade name of "ISOFOL24" from CONDEA Chemie GmbH. The (meth)acrylic acid derivatives include

an (meth)acrylic acid halide (e.g., (meth)acrylic acid chloride, (meth)acrylic acid bromide, etc.), an (meth)acrylate acid anhydride, and a short-chain alkyl (carbon number 1-4; such as methyl, ethyl, etc.) (meth)acrylate, preferably methyl (meth)acrylate. The esterification or transesterification is carried out with or without solvent.

[0145] For example, the esterification or transesterification with or without solvent is carried out as follows: Alcohol, polymerization inhibitor, (solvent), a catalyst and (meth)acrylic acid or its derivative described above, are charged in a reactor and are reacted under normal or reduced pressure at 70-140° C., preferably 100-120° C. The solvent is, for example, the above-mentioned aromatic solvent, mineral oil, and the like. Preferred solvents are benzene, toluene, xylene and the like, because using such solvent, it is easy to separate and remove by-products of water or lower alcohol. The polymerization inhibitor is, for example, a phenol compound (e.g., hydroquinone, hydroquinone monomethyl ether, p-benzoquinone, t-butyl cresol, catechol, etc.), phenothiazine, oxygen and air. These are used alone or together. The catalyst is for example, an acid catalyst (e.g., sulfuric acid, hydrochloric acid, p-toluenesulfonic acid, methanesulfonic acid, benzenesulfonic acid, xylene sulfonic acid, etc.) or a base catalyst (e.g., sodium hydroxide, potassium hydroxide, sodium alcoxide, etc.). The reaction liquid that the reaction was completed, is washed with water or aqueous alkali solution, if necessary, and refined removing the catalyst, the polymerization inhibitor or unreacted (meth)acrylic acid.

[0146] The homopolymer of the DTDA is prepared by the same process as the process of the (A11) homopolymer, mentioned above. The copolymer having the DTDA is prepared by the same process as the process of the copolymer (A) or (A11), mentioned above.

#### EXAMPLE

[0147] Having generally described the invention, a more complete understanding can be obtained with reference to certain specific examples, which are included for purposes of illustration only and are not intended to limit the scope of the present invention.

[0148] In the following examples, parts represents parts by weight.

#### DTDA SYNTHESIS

[0149] Into a 2 liter reaction vessel equipped with a thermometer, a stirrer, a dehydrator, a condenser, an air inlet tube, a nitrogen gas inlet tube, and a dropping funnel, 1000 parts of an "ISOFOL 24," 1.1 parts of a hydroquinone and 4 parts of a concentrated sulfuric acid were charged, 315.8 parts of methacrylic acid were added dropwise into the reaction mixture, over two hours, at the temperature 90° C., with bubbling air at gas flow for 25 ml/min. Simultaneously, the vessel was warming, so that the reaction mixture reached 120° C. when the addition was completed. The mixture was maintained at 120° C. for two hours to complete the esterification. Reducing the pressure to 4 kPa from atmospheric pressures, at 125° C., the unreacted methacrylic acid was removed. Then, 32 parts of 10% sodium hydroxide water solutions were added with stirring under less than 30° C., to neutralize the solution. Then, the upper layer was separated from the lower layer. In the upper layer including crude

2-decyl-tetradecyl methacrylate, five parts of an adsorbent "KYOWAAD-SOUSHI" (Kyowa chemical industry Co., Ltd.) were added and stirred for 60 min., at 60° C., then containing water was removed by evaporation. The product was separated from the solid impurities by filtration. The 1,100 parts of 2-decyl tetradecyl methacrylate was obtained. The solidifying point was -33° C. to -35° C.

[0150] FIG. 1 shows a <sup>1</sup>H-NMR spectrogram of the product, FIG. 2 shows a <sup>13</sup>C-NMR spectrogram of the product, and FIG. 3 shows an IR absorption spectrogram of the product.

[0151] Referring to the FIG. 1, the spectrogram shows following resonance peaks, shapes, coupling constants and the number of hydrogen atoms: 1H-NMR (CDCl<sub>3</sub>, 300 MHz): δ 6.08 (s, 1H), 5.52 (s, 1H), 4.04 (d, J=6 Hz, 2H), 1.93 (s, 3H), 1.6-1.7 (m, 1H), 1.1-1.4 (m, 40H), 0.87 (t, J=6 Hz, 6H). Referring to the FIG. 2, the spectrogram shows following resonance peaks: <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 300 MHz): δ 167.6, 136.7, 125.0, 67.3, 37.2, 31.8, 31.3, 29.8, 29.6, 29.5, 29.5, 29.3, 26.6, 22.5, 18.1, 13.9. Referring to the FIG. 3, the spectrogram shows following absorption frequency: IR (NaCl): 2924, 2855, 1720, 1639, 1466, 1319, 1296, 1165, 1013, 937, 814, 721 cm<sup>-1</sup>.

[0152] The 2-decyl tetradecyl acrylate is prepared by a similar process.

#### THE METHODS

[0153] [The method of measuring a Mw for the copolymers]

[0154] Molecular weight distribution was measured by gel-permeation chromatography (GPC). The conditions for the measurement were as follows:

[0155] Apparatus: HLC-802A, (Toyo Soda Co., Ltd.)

[0156] Column: TSKgel-GMH6, (Toyo Soda Co., Ltd.) connecting two columns in series

[0157] Column Temperature: 40° C.

[0158] Specimen (Sample solution): 0.5 weight % tetrahydrofuran (THF) solution

[0159] Injection amount of specimen: 200 micro L

[0160] Detector: a refractive index detector

[0161] In addition, the calibration curve of molecular weight was prepared to use polystyrene as a reference standard.

[0162] [The method of measuring a low-temperature viscosity]

[0163] The low-temperature viscosity was measured following JPI-SS-26-85 at -40° C.

[0164] [The method of measuring a V]

[0165] The viscosity index was measured following JIS-K-2283.

[0166] [The method of measuring a shear stability]

[0167] The shear stability was measured according to JASO M347-95, the period of test time was 12 hours. In addition, the liquid level is adjusted every three hours.

#### HOMOPOLYMER

[0168] The monomers listed in the Table 1 were polymerized following the above-mentioned method of the homopolymerization, and obtained the homopolymers. The crystallizing initiation temperature of the homopolymers is shown in table 1.

TABLE 1

Monomer	Tc (° C.) of homopolymer
a1-1 2-decyl-tetradecyl methacrylate	-30
a1-2 2-dodecyl-hexadecyl methacrylate	-14
a1-3 2-decyl-tetradecyloxyethyl methacrylate	-25
a3-1 2-ethylhexyl methacrylate	<-40 (*1)
a5-1 n-dodecyl methacrylate	-45

(\*1) less than -40° C.

[0169] Except for the homopolymer consisting the units of (a5-1), the other homopolymers have Tc of less than 5° C.

#### COPOLYMER PREPARATION

Example 1-9, Example 51, and Comparative Example 1-3

[0170] Into a reaction vessel equipped with a stirrer, a heating and cooling device, a thermometer, a dropping funnel and a nitrogen gas inlet tube, 25 parts of a toluene was charged. After the atmosphere in the vessel is replaced with nitrogen gas, the solution consisting of the listed amount (parts) of the listed monomer, DM and ADVN, in the table 2, was added dropwise from the dropping funnel. This addition was made over a period of 4 hours, at 85° C., in the absence of air. Further the reaction mixture was stirred at 85° C. for 2 hours, so that the polymerization proceeds well. Thereafter, toluene was evaporated under reduced pressure at 130° C., for 3 hours. The copolymers (A-1) to (A-9), (B-1) and (X-1) to (X-3), were obtained. The physical property of the copolymers are shown in table 3.

TABLE 2

	Copolymer	Monomer												D	AD
		name	a1-1	a1-2	a1-3	a2-1	a5-1	a2-1	a4-1	a4-2	a3-2	d-1	d-2	M	VN
Example	1	A-1	32					36	30			2		0.9	0.5
	2	A-2		20				36	12		32			0.9	0.5
	3	A-3			20			32	10		38			0.9	0.5
	4	A-4	30					38	32					0.9	0.5
	5	A-5		20				38	12		30			0.9	0.5
	6	A-6	20					30			50			0.9	0.5
	7	A-7	30	10				32			23		2	0.9	0.5
	8	A-8	30					32	35					0.3	0.5
	9	A-9						20	10			70		0.9	0.5
C. Example	51	B-1								20	80			0.3	0.4
	1	X-1				48					50	2		0.9	0.5
	2	X-2						52			45			0.9	0.5
	3	X-3					40	30	30					0.9	0.5

a2-1: methyl methacrylate

a4-1: n-hexadecyl methacrylate

a4-2: n-octadecyl methacrylate

a3-2: n-dodecyl methacrylate

d-1: N,N-dimethyl aminoethyl methacrylate

d-2: N,N-diethyl amino ethyl methacrylate

[0171]

TABLE 3

		Copolymer name	Mw ( $\times 10^3$ )	SI*	Tc ( $^{\circ}$ C.)	F	HLB
Example	1	A-1	2	9.2	<40 C. (*)	7.2	3.1
	2	A-2	3	9.2	<40 C.	6.6	3.2
	3	A-3	3	9.2	<40 C.	5.6	3.2
	4	A-4	3	9.2	<40 C.	6.6	3.1
	5	A-5	3	9.3	<40 C.	6.2	3.2
	6	A-6	3	9.2	<40 C.	8.0	3.0
	7	A-7	7	9.2	<40 C.	7.9	3.1
	8	A-8	6	9.2	<40 C.	7.7	3.1
	9	A-9	3	9.2	<40 C.	9.1	2.7
	51	B-1	6	9.0	-17	15.0	1.9
C. Example	1	X-1	2	9.0	<40 C.	25.0	2.5
	2	X-2	3	9.5	<40 C.	3.7	4.5
	3	X-3	3	9.2	19	6.0	2.7

(\*) less than 40 $^{\circ}$  C.

[0172] The copolymer (B-1) of the above Example 51 was an another copolymer that adding together with the VII of the present invention ((A-1) to (A-9)) into base oil.

## VII CONCENTRATES

[0173] 65 parts of each of the copolymers (A-1) to (A-9) and (X-1) to (X-3) was dissolved in 35 parts of the mineral

kinematic viscosity at 100 $^{\circ}$  C. of 6.0 $\pm$ 0.1 mm $^2$ /s, and also becoming the final lube oil composition of 100 parts. The lube oil compositions (10-18) of the present invention and the composition of the comparative example (4-6) were obtained. The VI, low temperature viscosity at -40 $^{\circ}$  C. and shear stability of the resultant compositions are given in table 4.

TABLE 4

		Amount of VII concentrate (gnt)	Copolymer name	VI	Low Temp. Viscosity (mPa $\cdot$ s)	Shear Stability (%)
Example	10	17	A-1	229	9900	10
	11	17	A-2	237	10000	10
	12	17	A-3	231	10000	10
	13	17	A-4	252	9700	10
	14	17	A-5	232	9900	10
	15	17	A-6	279	8800	10
	16	17	A-7	228	9900	10
	17	13	A-8	263	7200	25
	18	17	A-9	218	7000	11
	4	17	X-1	206	11000	—
C. Example	5	Not dissolved	X-2	—	—	—
	6	17	X-3	231	>90,000 (*)	10

(\*) more than 400,000 mPa  $\cdot$  s

oil (solvent refining oil; kinematic viscosity at 100 $^{\circ}$  C. 2.4 mm $^2$ /s). The VII concentrates were obtained.

[0174] 65 parts of the copolymer (B-1) was dissolved in 35 parts of the same mineral oil as the above. The copolymer concentrate was obtained.

## LUBE OIL COMPOSITION

Example 10-18, Comparative Example 4-6

[0175] Into a container made by the stainless steel equipped with a stirrer, 0.5 parts concentrate of the (B-1) were charged. Each of the concentrates of (A-1) to (A-9) and (X-1) to (X-3) and base oil (kinematic viscosity at 100 $^{\circ}$  C., 3.0 mm $^2$ /s, a viscosity index, 117) was added respectively, so as to becoming the final lube oil composition has a

## LUBE OIL COMPOSITION

Example 19-27, Comparative Example 7-9

[0177] The procedure same as the Example 10 was repeated with the exception that the final lube oil composition has a kinematic viscosity at 100 $^{\circ}$  C. of 5.0 $\pm$ 0.1 mm $^2$ /s. The lube oil compositions (19-27) of the present invention

and the composition of the comparative example (7-9) were obtained. The VI, low-temperature viscosity at  $-40^{\circ}\text{C}$ . and shear stability of the resultant composition are given in table 5.

TABLE 5

	Amount of VII concentrate (part)	Copolymer name	VI	Low Temp Viscosity (mPa · s)	Shear Stability (%)	
Example	19	13	A-1	216	5700	9
	20	13	A-2	218	6000	9
	21	12	A-3	217	6000	9
	22	12	A-4	218	5500	9
	23	12	A-5	218	5600	9
	24	12	A-6	216	5200	9
	25	12	A-7	215	5700	9
	26	10	A-8	243	4000	10
	27	12	A-9	204	4800	10
C.Example	7	12	N-1	195	6600	12
	8	Not dissolved	N-2	—	—	—
	9	12	N-3	217	>400,000 (*1)	9

(\*)1 more than 400,000 mPa · s

[0178] Similar result as the series of the experiments of table 4 was obtained.

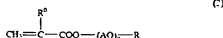
What is claimed as new and desired to be secured by letters patent is:

1. A viscosity index improver, which comprises a polymer (A) having a solubility parameter of 8.6-9.4, a crystallizing initiation temperature of equal to or less than  $-15^{\circ}\text{C}$ ., and a steric hindrance factor (F) of 0-13, said factor F being defined by the following equation:

$$F=4X+Y \quad (1)$$

wherein X and Y represent the total numbers of atoms at the 6th position and the 7th position, respectively, in the side chains, counted from the backbone; said polymer (A) having a weight-average molecular weight of 5,000-2,000,000 and comprising units of at least one monomer selected from the group consisting of:

(a) a monomer represented by the general formula:



wherein  $\text{R}^a$  is hydrogen atom or methyl group, R is a  $\text{C}_{1-20}$ alkyl group, n is 0 or an integer of 1-20 giving 0-10 on average. A is an alkylene group containing 2-4 carbon atoms, plural A's in case of n being at least 2 are the same or different, and the polyoxyalkylene moiety (AO), in case of the plural A's being different comprises random-wise or block-wise distributed oxyalkylene groups:

(b) an alkyl alkenyl ether;

(c) an alkenyl carboxylate; and

(d) a nitrogen-containing unsaturated monomer.

2. The improver of claim 1, wherein said polymer (A) contains units of said monomer (a), said monomer (b) or said monomers (a) and (b) in an amount of at least 30% by weight, with or without 0-45% by weight of units of said

monomer (c), 0-12% by weight of units of said monomer (d) and 0-20% by weight of units of another monomer.

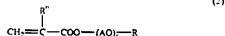
3. The improver of claim 1, wherein said polymer (A) is a copolymer (A1), comprising units of at least one monomer (a1) represented by the general formula (2) wherein R is a branched alkyl group containing 16-40 carbon atoms.

4. The improver of claim 3, wherein said copolymer (A1) comprises 5-90% by weight of units of said monomer (a1), and 10-60% by weight of units of an alkyl acrylate or methacrylate (a2) containing 1-4 carbon atoms in the alkyl group, with or without 0-85% by weight of units of at least one selected from the group consisting of an alkyl acrylate or methacrylate (a3) containing 8-15 carbon atoms in the alkyl group and a straight-chain alkyl acrylate or methacrylate (a4) containing 16-18 carbon atoms in the alkyl group.

5. The improver of claim 4, wherein said copolymer (A1) further comprises 0.1-10% by weight of units of said monomer (d).

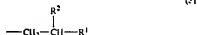
6. The improver of claim 5, wherein said monomer (d) is at least one selected from the group consisting of dimethylaminoethyl acrylate, diethylaminoethyl acrylate, morpholinoethyl acrylate, and corresponding methacrylates.

7. A viscosity index improver, which comprises a copolymer (A11) having a weight-average molecular weight of 5,000-2,000,000, comprising 5-90% by weight of units of at least one monomer (a1) and 5-95% by weight of units of at least one alkyl acrylate or methacrylate other than said monomer (a11); said monomer (a11) being capable of providing a homopolymer having a crystallizing initiation temperature of equal to or less than  $5^{\circ}\text{C}$ . and represented by the general formula:



wherein  $R^0$  is hydrogen atom or methyl group, R is a branched alkyl group containing 20-40 carbon atoms, n is 0 or an integer of 1-20 giving 0-10 on average, A is an alkylene group containing 2-4 carbon atoms, plural A's in case of n being at least 2 are the same or different, and the polyoxyalkylene moiety (AO), in case of the plural A's being different comprises random-wise or block-wise distributed oxyalkylene groups.

8. The improver of claim 7, wherein R is represented by the general formula:



wherein  $R^1$  and  $R^2$  are the same or different straight-chain alkyl groups containing 8-18 carbon atoms.

9. The improver of claim 7, wherein said copolymer (A11) has a solubility parameter of 8.6-9.4, a crystallizing initiation temperature of equal to or less than  $-15^\circ\text{C}$ , and a steric hindrance factor F of 0-13, said factor being defined by the following equation:

$$F=4X+Y \quad (II)$$

wherein X and Y represent the total numbers of atoms at the 6th position and the 7th position, respectively, in the side chains, counted from the backbone.

10. The improver of claim 9, wherein said copolymer (A11) has a steric hindrance factor F of 0-10.

11. The improver of claim 7, wherein said copolymer (A11) comprises 5-90% by weight of units of said monomer (a11), and 10-60% by weight of units of an alkyl acrylate or methacrylate (a2) containing 1-4 carbon atoms in the alkyl group, with or without 0-85% by weight of units of at least one selected from the group consisting of an alkyl acrylate or methacrylate (a3) containing 8-15 carbon atoms in the alkyl group, a branched alkyl acrylate or methacrylate (a12) containing 16-19 carbon atoms in the alkyl group, a straight-chain alkyl acrylate or methacrylate (a4) containing 16-18 carbon atoms in the alkyl group and a straight-chain alkyl acrylate or methacrylate (a5) containing 20-40 carbon atoms in the alkyl group.

12. The improver of claim 7, wherein said copolymer (A11) comprises 10-45% by weight of units of 2-decyl-

tetradecyl methacrylate, 20-45% by weight of units of methyl methacrylate, and 10-60% by weight of units of a straight-chain alkyl acrylate or methacrylate containing 10-18 carbon atoms in the alkyl group.

13. The improver of claim 7, wherein said copolymer (A11) further comprises 0.1-10% by weight of units of a nitrogen-containing unsaturated monomer (d).

14. The improver of claim 13, wherein said monomer (d) is at least one selected from the group consisting of N,N-dimethylaminoethyl acrylate, N,N-diethylaminoethyl acrylate, morpholinomethyl acrylate, and corresponding methacrylates.

15. A viscosity improver concentrate, which comprises 10-90% by weight of said improver of claim 1 and 10-90% by weight of a diluent.

16. A viscosity improver concentrate, which comprises 10-90% by weight of said improver of claim 7, and 10-90% by weight of a diluent.

17. A lube oil composition, which comprises a major amount of a base oil and 0.5-30% by weight of said improver of claim 1.

18. The composition of claim 17, wherein the base oil has a kinematic viscosity of 1-15  $\text{mm}^2/\text{s}$  at  $100^\circ\text{C}$ , and a viscosity index of at least 80.

19. A lube oil composition, which comprises a major amount of a base oil and 0.5-30% by weight of said improver of claim 7.

20. The composition of claim 19, wherein the base oil has a kinematic viscosity of 1-15  $\text{mm}^2/\text{s}$  at  $100^\circ\text{C}$ , and a viscosity index of at least 80.

21. A compound of 2-decyl-tetradecyl methacrylate.

22. A compound of 2-decyl-tetradecyl acrylate.

23. A homopolymer having a weight-average molecular weight of 5,000-2,000,000, comprises units of a compound selecting from the group consisting of the compound of claim 21 and the compound of claim 22.

24. A copolymer, having a weight-average molecular weight of 5,000-2,000,000, comprises 5-90% by weight of units of a compound selecting from the group consisting of the compound of claim 21 and the compound of claim 22, and 5-95% by weight of units of at least one monomer selecting from the group consisting of: an alkyl methacrylate or an alkyl acrylate other than the compound of claim 21 or claim 22; an alkyl alkenyl ether; an alkenyl carboxylate; and a nitrogen-containing unsaturated monomer.

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